



# **A Literature Review on The Behaviour of Buried Contaminated Concrete Over Time and Relevance to Plutonium, Americium and Uranium Contamination at The Rocky Flats Environmental Technology Site.**

Submitted to

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## Executive Summary

This report reviews current literature on the behaviour of plutonium, uranium and americium in contaminated concrete with relevance to surface contaminated concrete at the Rocky Flats Environmental Technology Site (RFETS). This review will be used in the second part of the project to design a draft work plan to more fully understand the mobility of this contamination at RFETS for the purpose of assessing radiologic risk over a period of 1000 years. The aim of the overall project is to provide a comparison of the behaviour of plutonium, uranium and americium present in contaminated concrete to that present in soils for which risk criteria are defined. The project will also establish what concentration of these radionuclides can be bound in concrete at RFETS that will be protective of water quality standards.

A review of literature on cement and concrete degradation, radionuclide leaching from cement and concrete, and plutonium, uranium and americium solubility and sorption under cementitious conditions has been undertaken. Sufficient information is available in the literature and in the RFETS Sitewide Geoscience Characterization study to qualitatively predict the degradation behaviour of concrete rubble at RFETS and to provide background information for evaluating the chemical controls on leaching, solubility and sorption of plutonium, uranium and americium. The main process of degradation affecting the predominant surface contamination of RFETS concrete is likely to be carbonation, the reaction with carbon dioxide either in soil gases or dissolved in groundwater. Attack by sulphate and processes controlled by microbial activity may also be relevant, but the involvement of these processes is more uncertain at present. Corrosion of steel rebar is also likely to contribute to the cracking of concrete blocks. The main form of degradation by carbonation is unlikely to result in disaggregation of the surface and may in fact result in a more resistant surface which is less prone to freeze-thaw and mechanical erosion. Formation of silica and iron hydroxide colloids is possible during degradation which could influence the migration of actinides.

Carbonation of the surface zone containing plutonium, uranium and americium contamination has important implications for the chemical controlled leaching of radionuclides. The local fluid pH surrounding the contamination will be lowered from above 12 to ~ 8 by carbonation. Redox (Eh) condition will be unaffected by carbonation and may not be changed from that of the background geochemistry, steel corrosion is the only likely mechanism by which reducing conditions may be established. It is emphasised that these conditions are not typical of the extreme high pH, low Eh deliberately engineered in radioactive waste repository designs and thus plutonium, uranium and americium are likely to be more mobile in RFETS concrete than in such repositories.

Experimental studies of leaching of plutonium, uranium and americium from cementitious materials are very limited. This is largely a result of the low mobility of actinides under these conditions, and the need for long time scale experiments. Data that is available would confirm the proposition that liquid contamination as well as particulate contamination is very close to the surface. Under these circumstances diffusive control is less important as the contamination will be in close contact with groundwater. Leaching from surface contamination is considered to be controlled by processes of sorption onto the degraded cement surface and, where concentrations are sufficiently high, by solubility control from a solid contaminant (e.g.  $\text{PuO}_2$ ). In view of this, a review of literature on plutonium, uranium and americium solubility and sorption under conditions in the degraded concrete surface has been undertaken. A substantial amount of literature is available concerning the solubility of actinides under cementitious conditions, although the majority of these studies are concerned

with higher pH's than relevant here, a good understanding of the controls on solubility and sorption is possible. An important factor controlling solubility, and hence release is the nature and solubility of the actinide contamination. Sorption distribution coefficients ( $R_{ds}$  or  $K_{ds}$ ) for actinides under high pH conditions are quite well defined, but again these mainly relate to high pH, non-carbonated cement substrates. Actinide sorption is generally less effective at lower pH, and uncertainties exist in the sorption mechanism on carbonated cements and on the uptake of contaminants by calcium carbonate.

In summary, a reasonable understanding of the degradation of concrete at RFETS is possible, the question of the mobility of plutonium, uranium and americium under the chemical conditions established in the degraded concrete is more uncertain. These contaminants are likely to be solubility controlled in the very near surface of the degraded concrete, however the nature and solubility limit of the solid contaminant phases are unknown.

## Introduction

This report comprises a review of the literature on processes relevant to the mobility of the radionuclides plutonium, uranium and americium present in contaminated concrete present at the Rocky Flats Environmental Technology site (RFETS). It has been suggested, for the purposes of assessing radiological risk, that release of radionuclides from contaminated concrete rubble remaining after decommissioning activities at RFETS will be similar to that from release from soil over a 1,000 year period (RMRS, 1998). On this basis a possible radiation dose based standard for determining the concentration of contaminants in concrete is the Tier 1 soil action level defined in the Rocky Flats Cleanup Agreement (RFCA) (DOE, 1998). Another possible standard is that radionuclides leached from concrete will be protective of water quality defined by Tier 1 action levels for ground water, Pu, Am 15 pCi/L, U 100 pCi/L (DOE, 1998, Attachment 5).

The aims of this project as defined in the statement of work (RMRS, 1998) is to provide a qualitative assessment of the physical and chemical properties of plutonium, americium and uranium contamination in concrete and to answer the questions

"Does concrete behave like soils at RFETS over the 1,000 year assessment period?"

"What concentration of plutonium, americium and uranium may be bound in concrete left at RFETS after decommissioning that will be protective of water quality standards?"

This literature review is the first stage of this exercise, the objectives of the review are to provide a preliminary understanding of the processes involved in concrete degradation and plutonium, americium and uranium leaching from concrete, at RFETS. This review includes examination of site specific data provided principally in the Groundwater Geochemistry Report for the RFETS (EG&G, 1995), together with verbal descriptions of the nature of the contamination in concrete from RMRS and Kaiser-Hill staff. A qualitative description of the degradation of concrete at RFETS and the chemical factors governing the mobility of plutonium, americium and uranium are provided. Comments are made on current inadequacies in the open literature in understanding processes of actinide mobility from contaminated concrete at RFETS.

In the second stage of the project gaps in the literature will be defined and a draft work plan will be designed to fill missing data and to test the environmental effects of concrete behaviour in the environment. In the draft work plan report, a conceptual model of the release of plutonium, americium and uranium from concrete left at

RFETS will be produced Available literature data will be used to assess the concentration of these radionuclides within contaminated concrete that are protective of water quality

### ***Overview of radionuclide/cement literature***

An extensive amount of literature exists in peer-reviewed journals, conference proceedings and in reports of various agencies and research institutes on the application of cement and concrete to the disposal of radioactive waste Cement-based materials are used commonly for the encapsulation of low- and intermediate-level waste and for proposed backfill material in repository designs Concrete is used extensively in the structural design of radioactive waste repositories Cement and concrete form a low permeability barrier to the ingress of groundwater to radioactive waste In addition, the high pH and high surface area of the cement matrix provides a chemical barrier to radionuclides, providing retardation by sorption and lowering solubility To understand the behaviour of this chemical barrier extensive research has been carried out to predict the evolution of chemical conditions in cement pore water over very long periods of time (100,000 years) Much of this research has concentrated on predicting pH during leaching of cement by groundwater as this is an important parameter controlling both the solubility and sorption of radionuclides Other areas of cement degradation, which impact on the structural integrity of concrete are attack by chloride, sulphate and magnesium, which can be at high concentrations in deep subsurface brines The microbial promoted attack of concrete is also quite frequently discussed in the radioactive waste literature

Measurement of leaching rate of certain radionuclides from cement wasteforms has been carried out Quite extensive experimental studies have been made of Cs, Co, Sr, I, C leaching (Amoya and Suzuki, 1992, Krishnamoorthy et al, 1992, Plecas et al, 1992b, Miyamoto et al, 1993, Nishi et al, 1991, Kato et al, 1996, Peric et al, 1993, 1994, 1995) and models based on diffusive transport of these relatively mobile elements have been developed (Plecas et al 1992a, Kim et al, 1992, 1993, 1996) Such data and models are not particularly relevant to the leaching of contaminants from RFETS concrete, here the contamination is in the form of Pu, Am and U, and the surficial nature of the contamination will not be influenced by diffusive properties of the cement matrix

Studies of the leaching of actinides from cementitious materials are much more limited, this in part reflects the very low mobility of actinides in cementitious systems, with the consequence that experimental time scales have to be extremely long In addition, the focus of this limited work has been concerned with the leaching of radionuclides from cement-encapsulated waste, rather than surface contamination Diffusion measurements do however provide a useful indicator of the depth to which actinides can penetrate into concrete

Despite the lack of data explicitly dealing with actinide leaching from concrete, there is another avenue to be explored Due to the use and proposed use of cementitious material for the immobilisation of radioactive waste, properties of radionuclides in cement environments have been extensively studied Thus solubilities of actinides in cement leachates have been determined, and sorption onto cement pastes have been measured Although these do not, on the face of it, appear to be directly relevant to RFETS leach behaviour, these experiments may in fact reveal useful information about the leaching of radionuclides from cements

As a consequence of the literature search criteria used, and the number of references related to radioactive waste disposal, many references examined relate to the use of cement based materials in repository designs and waste encapsulation It should perhaps be emphasised at this stage that although the literature reviewed is

sourced largely from such repository studies, the processes controlling plutonium, americium and uranium mobility at RFETS are not typical of those in radioactive waste repositories. In particular

- Contamination in RFETS concrete is surficial and will be in close contact with groundwater
- pH will be significantly lower than in engineered repositories, where it forms an integral part of the multi-barrier approach

### ***Literature search criteria***

The literature search was carried out using BNFL's Information Retrieval Service. The following databases were searched:

BIOSIS Previews	CA SEARCH (Chemical Abstracts)
CAB ABSTRACTS	Ceramic Abstracts
Chemical Engineering and Biotechnology Abstracts	Derwent World Patents Index
DIALOG SourceOne Engineering	Dissertation Abstracts Online
Ei Compendex Plus	Electric Power Database
EMBASE	Energy, Science and Technology (DOE)
Envrioline	FLUIDEX
GeoArchive	GEOBASE
GeoRef	Inside conferences
INSPEC	JICST - Eplus
Life Sciences Collection	METADEx
NTIS	Nuclear Science Abstracts
PASCAL	SciSearch
SPIN	TOXLINE
TRIS	Wilson Applied Science
World Translations Index	

The following keyword searches were made:

- 1 Cement or concrete and leach and radionuclide (192 returns)
- 2 Cement or concrete and degradation (156 returns)
- 3 Concrete and contamination and radionuclides or uranium or plutonium or fission product or nuclear waste or radioactive waste (95 returns)

These searches were selected so that the key publications on radionuclide mobility in cementitious radioactive waste systems would be covered, the relevance of these publications was determined as site specific data was received from RMRS. The last search concerning concrete contamination was the least successful and references here mainly concerned decontamination methods, contamination associated with nuclear reactors and nuclear fall out. On the basis of document title and available abstracts 60 papers and documents were chosen as being relevant and were obtained from the British Lending Library. In addition to these references a number of other sources of literature were examined which included

- 1 Materials Research Society Symposia "Scientific Basis for Nuclear Waste Management" VIII-XXI (1985-1998)
- 2 A collection of references on actinide solubility and sorption

In addition reference lists in reviewed publications were examined for further relevant references. A list of all references used in this review is provided in the Bibliography.

## Nature of Contamination of Rocky Flats Concrete

Information regarding the nature of contamination of construction concrete at RFETS is limited and no documented descriptions were available. Verbal descriptions of the nature of the contamination were provided at two meetings (Roberts, personal communication, Ervin, personal communication). Contamination of RFETS construction concrete by Pu, U and Am is thought to be present in three forms:

- Surface contamination of very fine grained  $\text{PuO}_2$  from a plutonium fire
- Contamination from Pu nitrate solution seepage through concrete
- Uranium present in locally derived aggregate used in concrete

The surface contaminated Pu is thought to be the most important for discussion here since contamination by Pu nitrate may be at levels too high for in-situ disposal. Plutonium is likely to be present in the chemically stable form  $\text{PuO}_2$ , as very fine-grained smoke particles resulting from combustion of Pu metal (Carnall and Choppin, 1983). Surface deposited  $\text{PuO}_2$  particulates in concrete are generally likely to be limited to the first few millimetres (DoE, 1995). Uranium and americium are assumed to be present on the surface in a similar form to surficial Pu, although the nature of these compounds is more uncertain than for plutonium, uranium could be present as either  $\text{UO}_2$  or in the U(VI) oxidation state as hydrated phases (e.g. schoepite) if contamination is related to combustion, americium may be present as hydroxide. The depth of liquid nitrate contamination on RFETS concrete is not known. Experiments have however been performed on the attenuation of Pu and Am mobility in concrete immersed in nitrate (Jakubick, 1987) which show that at a steady state uptake from  $10^{-5}$  M Pu and  $10^{-6}$  M Am solutions both Pu and Am penetrated to a depth of around 2cm in concrete pre-treated with 3M nitric acid. Pu diffusion and leaching experiments reviewed in a later section indicate that diffusion is extremely slow. Liquid Pu nitrate contamination is therefore likely to be close to the surface, and thus will be influenced by chemical degradation of the concrete. Uranium in aggregate is present presumably at background levels in local bedrock. Uranium in aggregate is assumed to be evenly distributed through the concrete and its release will be controlled by the gross degradation of the concrete.

## Site Specific Geochemistry

The geochemistry and composition of the groundwater at RFETS is a crucial factor in determining the leaching behaviour of surface contaminated concrete. Therefore, a review of the groundwater geochemistry is appropriate. This review is based on the comprehensive site characterisation report (EG+G, 1995), and it has not been deemed necessary to offer any new interpretation. Rather, those factors of groundwater geochemistry



that are important, from a concrete leaching context, have been highlighted, extracted and assessed. The aim is to summarise the magnitude and variation of important parameters, in order for the literature review to be placed within a site specific context.

### ***Summary of Rocky Flats Geochemistry***

The hydrology of the RFETS site is divided into two distinct units, the Upper Hydrostratigraphic Unit (UHSU) and the Lower Hydrostratigraphic Unit (LHSU). The UHSU is composed of unconsolidated, surficial deposits and weathered sandstone of the underlying Laramie and Arapahoe formations. The LHSU consists of the unweathered portions of the Arapahoe and Laramie formations.

Groundwater flow is generally from west to east, with permeability and hydraulic conductivities greater in the UHSU than in the LHSU. There appears to be limited hydrological communication between the two units. The vertical hydraulic conductivity of the LHSU is an order of magnitude less than the horizontal conductivity, indicating that the LHSU acts as a hydraulic barrier to vertical groundwater flow.

The groundwater geochemistry report (EG&G, 1995) presents data from samples collected from 1990 and 1994, from 532 wells. The data is presented in terms of Stiff and Piper diagrams, and time series graphs. In addition, the results from geochemical modelling (using WATEQF) and inverse modelling/reaction path modelling (using NETPATH) are also shown and discussed.

In summary, the UHSU and LHSU comprise significant geochemical units, with the former predominantly calcium bicarbonate dominated and the latter considerably more varied, ranging from a sodium bicarbonate to sodium sulphate dominated groundwater. A major exception to these generalities is found in groundwaters close to the Operational Units, where contamination results in UHSU compositions as varied as LHSU waters, with sodium and sulphate particularly enhanced.

Data from wells along four proposed flow paths are also presented, and also interpreted through modelling. In general, the concentrations of major cations (Ca, Mg, Na and K) and total dissolved solids increase along the flow paths, which could be indicative of contamination, infiltration or mixing of groundwaters. However, inverse modelling suggests that the evolution of groundwater composition can be explained by natural geochemical reactions, such as dissolution and precipitation of mineral phases, and ion exchange reactions. In particular, the precipitation of kaolinite,  $\text{SiO}_2$  and iron minerals, the dissolution of calcite, pyrite, microcline and chlorite and exchange of calcium for sodium, would appear to be the more important mechanisms. The conclusion is that the mixing of additional groundwaters is not required to account for the evolution of major element geochemistry along the major flow paths.

However, local variations are shown to exist, particular along the Industrial Area flow path, where the major ion composition of the UHSU changes from a calcium bicarbonate water to a mixed sodium bicarbonate/sodium sulphate groundwater. In particular, groundwaters close to the Solar Evaporation Ponds indicate elevated levels of major cations, strontium, uranium-235, chloride and sulphate, while groundwaters close to the Landfill exhibit low pH's, potentially low Eh and elevated metal concentrations. It does not appear that these local variations are reflected in the overall geochemical evolution along the flow paths, as the groundwater at the end of the flow path is again a calcium bicarbonate water.

## ***Variations in Specific Parameters***

### **Carbonate**

Carbonation is an important degradation mechanism, which affects the physical and chemical integrity of concrete. Carbonate also affects the solubility and sorption of actinides in groundwater. As has been mentioned above, the groundwaters of the UHSU can be classified as calcium bicarbonate, with the carbonate level likely to be controlled by calcite solubility. Taking data from the Flow Path diagrams (Figures 5-8 to 5-17, EG&G, 1995), bicarbonate concentrations appear to vary from less than 1 mg/l in the background wells of the Southern Flow Path to 200 mg/l along the Woman Creek flow path. However, boreholes in the Industrial area exhibit concentrations much higher than this. For example the Stiff diagrams presented in Plate 2 (EG&G, 1995) show bicarbonate concentrations of 20 meq/l (equivalent to 1200 mg/l).

The Lower Hydrostratigraphic Unit exhibits lower bicarbonate levels, as shown in Figure 6-46 (EG&G, 1995), where a uniform concentration of 100 - 200 mg/l is observed site wide, apart from area around the Industrial Area, where concentrations rise to above 200 mg/l.

### **Sulphate**

Sulphate is an important anion producing enhanced degradation of concrete. Sulphate is also a potential microbial substrate, which could enhance concrete degradation and radionuclide mobility. Sulphate is generally low in the UHSU, typically less than 10 mg/l in the Woman Creek Flow Path background wells. In the Industrial area sulphate is much more variable increasing to over 1000 mg/l. The groundwater around the Solar Evaporation Ponds and Ponds B along the Walnut Creek appear to be particularly enhanced with respect to sulphate concentrations.

Figure 6-51 (EG&G, 1995) indicates that the concentration of sulphate in the LHSU is fairly constant across the site, less than 100 mg/l. This may indicate that the background concentrations of sulphate are slightly higher in the LHSU than in the UHSU. There are increases in the Industrial Area, but these do not appear to be as high as those in the UHSU.

### **Chloride**

Chloride produces enhanced degradation of concrete and induces corrosion of steel reinforcements (rebars). Chloride generally behaves like the other major elements, as concentration tends to increase along the flow paths. In the UHSU, background concentrations are less than 25 mg/l, while the concentrations at the RFETS plant are generally between 25 and 50 mg/l, with hot spots, again, around the industrial area (where concentrations exceed 500 mg/l in places). In the LHSU, concentration is fairly uniform at less than 50 mg/l.

### **Reduced Nitrogen, Sulphur and Organic Matter**

Reduced species are required for microbial degradation, and nitrogen, sulphur and carbon are often present as reduced species in soils and groundwater. There is no mention of reduced nitrogen, in the form of ammonium, in any of the groundwater analyses, which is reflected in the redox measurements (see later). Pyrite is present

in certain areas of the site, and this would appear to be only source of sulphide. Organic composition is less clear, and apart from anthropogenic organic compounds, the presence of organics is not mentioned.

## **pH**

pH is an important control on radionuclide mobility, and on alkali and Ca leaching of concrete. The background pH at the RFETS appears to be between 7.5 and 8, and appears to be fairly constant along all four flow paths, no doubt due to calcite equilibrium. The highest pH's occur around the Industrial Area, where the pH reaches values above 8. Groundwater close to the Landfill exhibits relatively low pH's (below 7). In general, there is relatively little pH variation over the site, in the UHSU. The isoconcentration map for the LHSU does indicate three areas where the pH is above 10. However, these appear to be isolated and the pH is otherwise below 8.

## **Redox**

The oxidation state of redox sensitive elements such as plutonium and uranium is important to their mobility. Redox measurements can also give an indication of the extent of microbial activity. The amount of redox data available from the site is sparse, and the difficulties in measuring Eh are acknowledged. The redox potentials were measured using a flow-through cell, and the resulting Eh's are in the range of 0.09 to 0.32 V, i.e. mildly oxidising. The presence of siderite and pyrite suggests reducing conditions, thus either there are pockets of anaerobic waters or, more likely, the presence of these minerals is indicative of the conditions in the past when these minerals were formed. It is mentioned that potentially low Eh's may be encountered close to the Landfill, but the values are not presented in the report.

# **Cement and Concrete Degradation**

## **Introduction**

Several physical, chemical and biological processes contribute to the degradation of cement and concrete (Lagerblad and Tragardh, 1996, Glasser, 1997, Rogers, 1993a). Many of the processes are inter dependant and involve some aspect of chemical degradation. Chemical degradation reactions of cement minerals are important as they control the local pore fluid chemistry where radionuclide contamination may exist. Fluid chemistry exerts a strong influence on the solubility of the actinides and in some cases radionuclides may co-precipitate with cement alteration products. Sorption of radionuclides is also influenced by fluid chemical conditions such as pH as well as the surface mineralogy. It is therefore necessary to review the major chemical reactions involved in cement and concrete degradation.

The main chemical processes affecting cement and concrete are

- Leaching and acid attack
- Carbonation
- Sulphate, magnesium and chloride attack
- Alkali-aggregate reactions
- Corrosion of steel rebars

Biodeterioration of concrete principally involving microbial induced attack facilitates localised chemical degradation by several processes leading to enhanced surface degradation of concrete. Since contamination in RFETS concrete is concentrated at the surface such processes operating at the groundwater interface must be considered to be potentially important in releasing radionuclides.

The mobility of radionuclides in groundwater can be enhanced by the presence of suspended particulate colloidal materials onto which radionuclides may be sorbed. Since concrete degradation may produce such fine-grained material available literature on colloid generation is considered.

An understanding of long-term degradation of concrete can be obtained from study of ancient analogues of modern concretes and from computer models. Computer models include prediction of the structural evolution of concrete repositories and the prediction of chemical degradation and pH evolution. Analogues and models provide an estimate of the time-scale of concrete degradation and the likely extent of degradation during the 1000-year assessment period.

Following review of the above aspects of cement and concrete degradation the processes most relevant to RFETS will be discussed with consideration to the nature of radionuclide contamination and site-specific groundwater conditions.

### ***Chemical evolution of cement minerals***

Hydration of Portland Cement (OPC) leads to the formation of a variety of chemical phases which make up hardened cement (Lea, 1980). The initial pore solutions formed on dissolving anhydrous OPC are strongly oversaturated and hydrated silicate phases form in equilibrium with the pore solution. The kinetics of hydrated OPC mineral formation is however slow, initial phases formed are amorphous gels which form more crystalline phases with accelerated ageing, and at increased temperature. The compositions of the initial gel hydration phases formed are variable and the sequence in which they form is partly dependent on temperature and curing conditions. During leaching by pure water, alkalis and calcium are removed from the cement minerals, which results in a decrease in pH of the cement pore fluid and change in composition of the cement matrix.

### **Hydrated cement minerals**

A standard nomenclature is used to abbreviate OPC and hydrated cement mineral formulae in most publications on cement and concrete.

Abbreviation	Oxide Formula
C	CaO
S	SiO <sub>2</sub>
A	Al <sub>2</sub> O <sub>3</sub>
F	Fe <sub>2</sub> O <sub>3</sub>
s	SO <sub>3</sub>
H	H <sub>2</sub> O

The symbols **m** and **t** are commonly used to denote the ratio of calcium in a mineral and correspond to mono- and tri- respectively e.g. monosulphate AFm

Some of the main hydration products are

- Calcium-silicate-hydrate (CSH) - the main component of hydrated OPC. Amorphous to semi-crystalline with Ca/Si molar ratio of 0.8 to 3.0, with variable water content. CSH forms during the hydration of anhydrous tri- or di- calcium silicate with water yielding  $\text{Ca}(\text{OH})_2$  and a more silica rich CSH.
- Calcium hydroxide - a crystalline product forming large crystals
- Aluminium-iron-mono (AFm) these phases have the general formula  $(\text{Ca}_2(\text{Al}, \text{Fe}) (\text{OH})_6 \text{X}_y \text{H}_2\text{O})$ , where X is an equivalent of a single charged anion. Monosulphate and Friedel's salt are important hydrated cement phases containing sulphate and chloride respectively.
- Tri-calcium-aluminates (Aft) formed by hydration of calcium aluminate, these phases can contain anions such as  $\text{SO}_4^-$  and  $\text{CO}_3^-$ . The sulphate mineral ettringite is an important member of this group, resulting in sulphate promoted degradation.
- Hydrogarnet - a solid solution series containing Ca, Si and Al, which coexists with CSH phases.
- Brucite ( $\text{Mg}(\text{OH})_2$ ) small amounts of this phase are present in hydrated cement. Secondary brucite is responsible for Mg promoted attack.

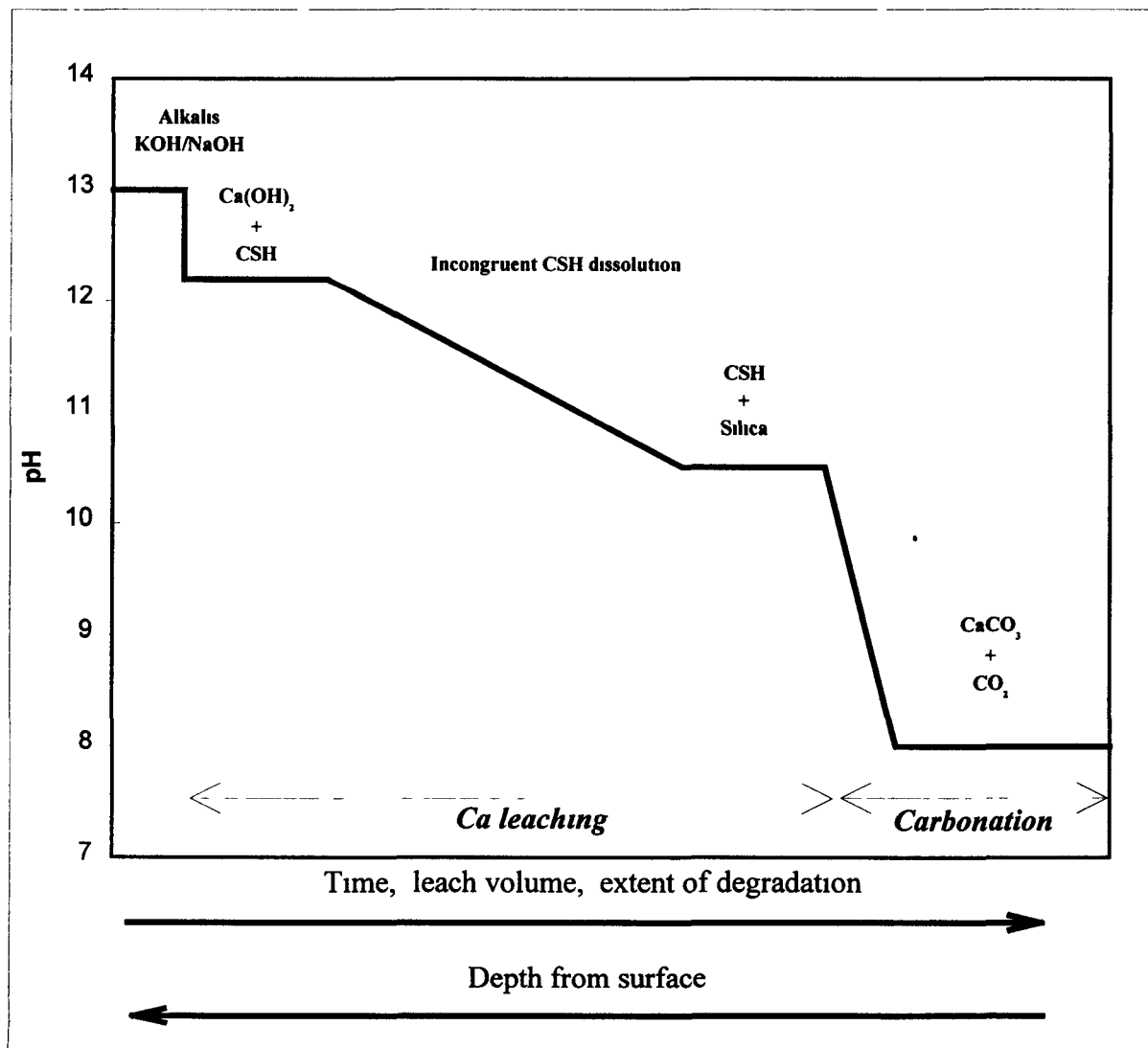
In pure OPC based concretes with low concentrations of reactive alumina, calcium hydroxide and CSH are the main phases present. Alumina containing phases are more important to applications of cement grouts and backfills used in the encapsulation of radioactive waste which include blast furnace slag and pulverised fly ash as additives, such materials contain a high content of pozzolanic reactive alumina which results in the formation of aluminous hydrated cement phases. Aggregate added to concrete may contain alumina in the form of rock forming minerals, however, these phases are largely unreactive.

### Leaching of $\text{Ca}(\text{OH})_2$ and CSH

Extensive experimental studies have been performed examining the leaching of  $\text{Ca}(\text{OH})_2$  and CSH in pure water (Berner, 1987, Adenot *et al*, 1992, Atkins *et al*, 1992a,b,c, 1994, Engkvist *et al*, 1996, Delagrave *et al*, 1997, Glasser, 1997, Bennett *et al*, 1992, Pfingsten and Shiotsuki, 1998, Duerden *et al*, 1997, Neall, 1996, Quillin *et al*, 1994). The majority of these studies have been performed to examine the pH behaviour during leaching which is an important control on the mobility of radionuclides from cement-based grouts and backfill materials. The leaching of OPC based cements can be divided into five main periods (Figure 1)

- Flushing of residual alkalis (NaOH and KOH) from pore spaces at pH 12-14
- Leaching in the presence of  $\text{Ca}(\text{OH})_2$  pH is buffered at over 12.0, CSH co-existing with  $\text{Ca}(\text{OH})_2$  has a Ca/Si ratio of approximately 1.8
- When  $\text{Ca}(\text{OH})_2$  is exhausted pH is controlled by the CSH phase which dissolves incongruently, preferentially releasing Ca into solution. pH decreases from over 12.0 to ~10.5 as CSH changes in composition from Ca/Si ratio 1.8 to 0.8
- On reaching a Ca/Si ratio of ~0.8 CSH dissolves congruently and pH remains constant at ~10.5 until the CSH finally dissolves
- Following dissolution of CSH pH is controlled by secondary Ca minerals, typically calcite under groundwater conditions. pH drops to ~7-8 dependent on carbonate levels in the groundwater

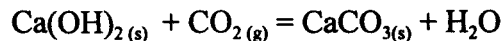
The duration of these pH buffers depends on the amount of each mineral in the concrete, the permeability (related to the quality of the concrete), and the groundwater chemical composition. The effect of alkalis is relatively short-lived since these are present in the initial porespace and are removed after flushing of 2-3 pore volumes. The amount of free  $\text{Ca}(\text{OH})_2$  is determined by the amount of pozzalanic material present in the concrete, excess  $\text{Ca}(\text{OH})_2$  reacts with such material forming CSH and CASH phases. Pure OPC concretes used for construction purposes, which do not contain blast furnace slag or pulverised fuel ash will contain significant amounts of free  $\text{Ca}(\text{OH})_2$ . CSH form the main buffering phase, the rate and duration of dissolution of Ca depend on temperature, surface area and the concentration of Ca, Si and carbonate in the groundwater. Dissolution is most rapid in soft  $\text{CO}_2$ -rich water, and slower in  $\text{CaCO}_3$  waters. Acidic water produced by microbial action, such as sulphide oxidation, or acidic spillage onto concrete will effectively accelerate the leaching process. Under accelerated acidic leaching diffusion processes limit the leaching process (Lefebvre, 1997). The sequence of changes in cement mineralogy occurring during leaching illustrated in Figure 1 can be considered to occur either as function of time, or fluid volume at a given point, or as function of distance representing zoned alteration of a concrete surface.



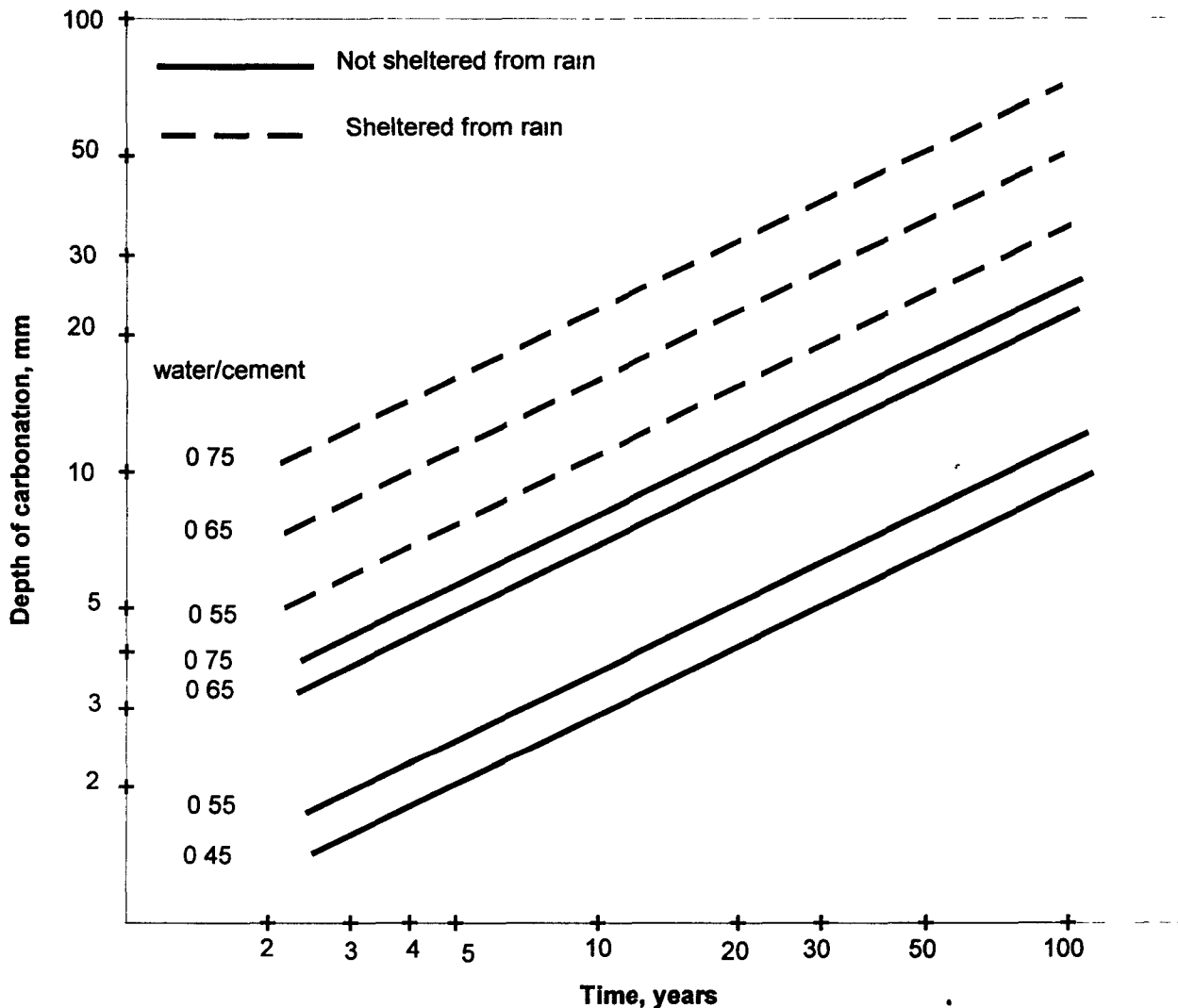
**Figure 1 Evolution of cement pore fluid pH during leaching**

## Carbonation

Carbon dioxide reacts strongly with the alkaline components of OPC concrete during the process of carbonation. Both  $\text{Ca(OH)}_2$  and CSH react with  $\text{CO}_2$  to form calcite.



Carbonation can occur in both saturated groundwater, in the unsaturated zone, and in above ground structures. In soils carbonation is favoured by high  $\text{CO}_2$  content and the humidity of the soil gas. Optimum humidities are around 75%RH (Houst, 1997), the carbonation reactions only occur in the presence of water, however water produced by carbonation must be allowed to diffuse out of the carbonated layer. Cement permeability and original water/cement ratio are therefore important to the extent of carbonation. Tuutti (1982) has investigated the effects of permeability on carbonation (Figure 2), in rainwater a good quality concrete with W/C 0.45 will carbonate to a depth of 5 mm in 50 years. In groundwater where  $\text{CO}_2$  levels are higher than in the atmosphere, carbonation will be more effective (Lagerblad & Tragardh, 1996).



**Figure 2 Measured mean carbonation depth in Portland cement concrete with varying water/cement ratios**  
**After Tuutti, (1982), Lagerblad & Tragardh, (1996)**

Formation of calcite from  $\text{Ca(OH)}_2$  results in an increase in volume of 12% (Houst, 1997) which reduces porosity. Despite a decrease in porosity overall shrinkage occurs (Houst, 1997) and microcracks develop (Walton *et al*, 1997). Decreases in porosity are beneficial in view of degradation by freeze-thaw mechanisms. Overall the durability of cement increases during carbonation. Carbonation results in a large decrease in pH to  $\sim 8$ , where steel reinforcement is more prone to corrosion and where microbial induced degradation may become established. Studies of contaminant leaching from carbonated cements show varied behaviour, some contaminants such as Sr are incorporated in the secondary calcite (Walton, *et al*, 1997, Curti, 1998) while unreactive species may show increased diffusion as a consequence of microcrack development (Walton *et al*, 1997), or lower diffusion in high w/c cements (Sarott *et al*, 1992).



## Sulphate, Magnesium and Chloride attack

Accelerated degradation of hardened OPC concrete occurs by the formation of secondary sulphate phases, by reaction of hydrated cement phases with groundwater sulphate. Formation of sulphate minerals results in a volume increase, which eventually produce expansion, and may result in fracturing and spallation of concrete. Ettringite is the sulphate phase most commonly associated with sulphate attack and forms by reaction of calcium aluminates and monosulphate ( $C_3A \text{ CaSO}_4 \cdot 12\text{H}_2\text{O}$ ) in OPC. Ettringite is a primary component of hydrated cement resulting from the inclusion of gypsum to control setting time. Secondary ettringite forms by further reaction of sulphate in groundwater. Sulphate-resisting cements are formulated which contain a low proportion of alumina to reduce ettringite formation in sulphate waters. At increased sulphate concentrations, gypsum ( $\text{CaSO}_4 \cdot \text{H}_2\text{O}$ ) forms by reaction of  $\text{Ca}(\text{OH})_2$ , in 5% sulphate solution ettringite and gypsum form concurrently (Ferraris et al 1997a). Expansion of cement exposed to sulphate solutions occurs initially by a diffusion controlled mechanism until available porespace is filled by gypsum and ettringite, cracking then follows which allows further access of sulphate solution to unreacted monosulphate (Pommersheim and Clifton, 1994).

In the presence of both sulphate and carbonate the mineral thaumasite ( $\text{CaSiO}_3 \cdot \text{CaCO}_3 \cdot \text{CaSO}_4 \cdot 15\text{H}_2\text{O}$ ) can form from alteration of CSH phases. Since CSH is the main binding agent in the cement this form of sulphate attack results in complete breakdown to a disintegrated mush (Crammond and Halliwell, 1997). Thaumasite attack is limited in occurrence and is favoured by low temperatures and use of limestone and in particular dolomite aggregate.

Magnesium sulphate solution is more deleterious to concrete than alkali sulphates because CSH phases are attacked as well as the aluminous phases. Under the high pH conditions of the cement pore fluid brucite ( $\text{Mg}(\text{OH})_2$ ) precipitates and lowers pH, so that the CSH is destabilised, CSH then forms gypsum and free silica as follows



There is a net expansion during this reaction which results in fracturing, the formation of brucite produces a hard skin on the surface of mortar and concrete and this can restrict further attack.

The extent to which sulphate attack will take place will depend on the sulphate concentration of percolating groundwater. Secondary ettringite will only form if the groundwater has a higher sulphate concentration than that of the cement equilibrated pore solution. The sulphate concentration of the cement porewater is controlled by temperature and alkali content (Lagerblad & Tragardh, 1996) and can vary between 0.1 and 100 mM/l  $\text{SO}_4^{2-}$  (Damidot *et al* 1992). No precise groundwater  $\text{SO}_4^{2-}$  concentration can be specified at which sulphate attack becomes significant. A significant loss of compressive strength occurs after one year's storage in 5% sulphate (Lea, 1980), while at a concentration of 0.5% sulphate magnesium sulphate attack is significant but sodium sulphate has little effect. Atkinson and Hearne (1990) have developed a mechanistic model to predict the long-term durability of concrete exposed to sulphate groundwater.

Chloride ions in groundwater can have a similar effect on concrete degradation as sulphate. Normal cements have very low chloride contents to avoid corrosion of steel reinforcement. Chloride ions bind to the AFm phase and produce Friedel's salt  $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CaCl}_2 \cdot 10\text{H}_2\text{O}$ , at very high concentrations of chloride the phase trichloride  $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaCl}_2 \cdot 32\text{H}_2\text{O}$  is formed. The action of chloride may also produce reactions in the

sulphate cement phases (Lagerblad & Tragardh, 1996) where chloride replaces sulphate in monosulphate which then is available to produce ettringite. Reactions among chloride and sulphate cement phases are dependant both on temperature and chloride content. The AFm chloride phase is stable between 10 and 1000 mmol/l Cl at 25°C (Atkins *et al*, 1994). Chloride concentrations of around 300 mmol/l and temperatures above 50°C are required to produce decomposition of ettringite (Lagerblad & Tragardh, 1996).

### **Alkali - aggregate reactions**

Quartz and other rock forming minerals are unstable under the strongly alkaline conditions produced by the presence of sodium and potassium hydroxide in concrete pore solutions. Crystalline minerals such as quartz are however slow to react even under strongly alkaline conditions. More reactive forms of silica such as opal, chalcedony and glassy acid to intermediate volcanic rocks are liable to react to form an alkali-silica gel and CSH. Formation of these phases as alteration rims around aggregates produces expansive forces, which may result in cracking (Ferraris *et al*, 1997b) and exudation of a soft viscous gel (Lea, 1980). Such alkali-aggregate reactions are dependent on the alkali content ( $\text{Na}_2\text{O} + \text{K}_2\text{O}$ ), below 0.6%  $\text{Na}_2\text{O}$  usually no deleterious alkali-silica reactions occur over short time-scales (100 years) (Lagerblad & Tragardh, 1996). Formation of alkali-silica gels removes alkali and lowers pH and this induces dissolution of  $\text{Ca}(\text{OH})_2$ , released Ca may then exchange with alkali-silica gel to release alkalis and induce further alkali-silica reaction (Wang and Gillot 1991, Lagerblad & Tragardh, 1996). The rate of alkali-aggregate reactions is controlled by the rate of diffusion of alkalis to the reaction site within the aggregate or on the aggregate surface and by the dissolution rate of silicates. Silicate dissolution rates are strongly pH dependent and increased at high pH (Lasaga, 1984). Contact of groundwater with concrete will clearly reduce the susceptibility for alkali-aggregate reactions by removing alkalis and lowering pH.

### **Corrosion of steel reinforcements**

Corrosion of steel reinforcement (rebars) results in expansion and ultimate fracturing of concrete. Formation of FeO from Fe results in doubling of volume, while the formation of ferric hydroxide ( $\text{Fe}(\text{OH})_3 \cdot 3\text{H}_2\text{O}$ ) increases volume by a factor of 6.5 (L1 and L1, 1997). Steel corrosion is thought to be limited under the high pH conditions due to the formation of a passivating protective surface (Wheat *et al*, 1997). Corrosion is induced in concrete by the effects of chloride and carbonation. Chloride-induced corrosion is generally considered more important (L1 and L1, 1997, Constantinou and Scrivener, 1997), largely because the effects of carbonation are slow.

A number of mechanisms are likely to be responsible for chloride-induced corrosion (summarised in Wheat *et al*, 1997), chloride may attack the protective film/substrate bond without attacking the passivating layer or the layer may be chemically attacked. Other theories propose that chloride is preferentially adsorbed in competition with dissolved oxygen and hydroxyl ions, or that chloride ions may penetrate the oxide film more easily than other ions. Once the passivating layer is broken galvanic corrosion occurs. Steel corrosion rapidly consumes dissolved oxygen and then produces hydrogen and establishes reducing conditions.

Carbonation-induced corrosion proceeds by lowering the pH of the concrete pore fluid below that at which a passivating layer forms. Although the rate of carbonation is affected by the quality of the concrete

(water/cement ratio), once corrosion is initiated the initial properties of the concrete have no effect (Constantinou and Scrivener, 1997)

## ***Biodeterioration of Concrete***

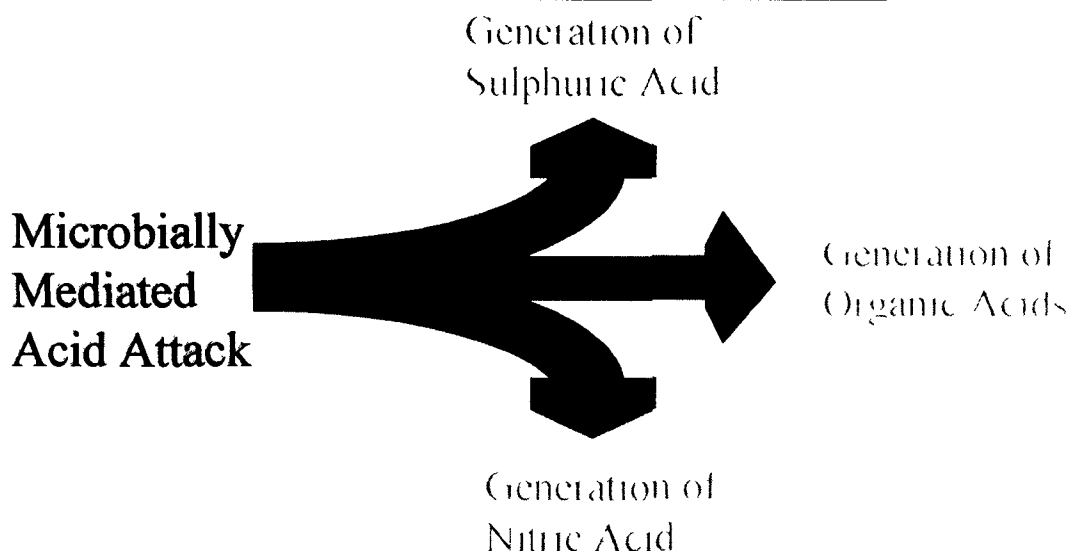
Biodeterioration can be defined as any undesirable changes in the properties of a material by the activity of organisms i.e. plants, animals and micro-organisms. In the specific case of concrete the organisms of interest are on the whole micro-organisms, and these organisms will be the focus of this section. Micro-organisms are ubiquitous in all natural and man made environments and have been associated with the deterioration of many commercially important materials including construction materials such as steel, stone and concrete. This chapter will describe the processes by which microbial biodeterioration of radioactively contaminated concrete can take place, present examples from other industries where appropriate and outline the factors which influence the rate and extent of biodeterioration.

### **Microbially Induced Degradation of Concrete and Cement**

Microbially induced degradation of cement based materials or MID has been extensively studied in the nuclear industry due to its potential role in the deterioration of containment in cemented waste forms (Rogers et al 1993a,b, 1994, 1996) and has even been developed into a biologically based decontamination process for surface contaminated concrete (Rogers et al, 1997). In non-nuclear industries MID has been associated with the degradation of sewage pipes, water distribution systems, power station cooling towers and buildings (Rogers 1993a).

MID has two main aspects, firstly the deterioration of the concrete surface by the action of micro-organisms resulting in a loss of structural integrity. This results in the surface of the concrete being susceptible to sloughing off carrying any associated radionuclides with it. Secondly micro-organisms have the ability to secrete complexing agent which may mobilise radionuclides which are weakly bound to the concrete. Once complexed in this manner these radionuclides are susceptible to further mobilisation via water flow for example.

Direct deterioration of the concrete surface occurs when micro-organisms growing on the surface of the concrete generate acidic compounds which attack the concrete in the same manner as chemical acid attack. The fact that in MID the process is microbially mediated usually results in the impact being more severe than direct chemical attack. This is because the micro-organisms grow in intimate contact with the surface and consequently any acid generated impacts on the surface as a concentrated point source. There are three well-known types of microbially mediated acid attack which are outlined in figure 3. The primary mode of acid attack is one of enhanced leaching where the inherent alkalinity of cement pore fluid is neutralised and alkalis and calcium are removed as soluble salts. The specific soluble salts formed depend on the specific acid involved in the attack.



**Figure 3 Types of Microbially Mediated Acid Attack**

The generation of sulphuric acid is catalysed by sulphur oxidising bacteria with bacteria from the genus *Thiobacilli* being most commonly associated with concrete degradation. *Thiobacilli* species get their energy for growth from the oxidation of reduced sulphur compounds with the subsequent generation of sulphuric acid. The majority of these bacteria use molecular oxygen to drive this oxidation but there are species which can use nitrate in the absence of oxygen. This group of bacteria has a wide tolerance to acidity with *Thiobacilli* species growing at pH's ranging from pH 6.5 to below pH 4.0 (Smith and Strohl 1991). The bacteria deposit sulphuric acid directly on the surface of the concrete as they grow. Since sulphuric acid will react with and destroys Portland cement at any temperature above freezing (Hall 1989) this form of MID can have a devastating effect on any concrete structure under attack. The result of sulphuric acid attack is a loss of granular structure and the formation of sulphate salts such as gypsum (Rogers et al 1993a). Sulphate may also be available for attack of AFm phases forming ettringite.

In order for *Thiobacilli* species to grow they require sources of oxygen, carbon dioxide and reduced sulphur. In nature the reduced sulphur source is generally found in the form of pyrite. Pyrite oxidation is commonly associated with a specific species of *Thiobacilli*, *Thiobacillus ferrooxidans*. This bacteria can oxidise both reduced iron and sulphide to generate energy for growth, and is the key species in the generation of acid mine drainage and microbial mining of metals such as copper and nickel (Brierley and Brierley 1997). In other cases *Thiobacilli* species may grow on reduced sulphur compounds generated by another group of bacteria, the sulphate reducing bacteria (SRB). This is important since it allows sulphuric acid based MID to occur where no obvious source of reduced sulphur exists. In this situation the sulphate reducing bacteria reduce sulphate to generate hydrogen sulphide as part of normal growth. This process occurs under strong reducing conditions, the sulphide generated then migrates into an oxidising environment where *Thiobacilli* species are able to utilise it generating sulphuric acid as a by-product. The classic example of this cycling of sulphur resulting in concrete degradation is in sewer systems. Here, SRB's are able to grow in the liquid waste in the bottom of the sewer pipes generating hydrogen sulphide. This migrates as a gas into the body of the sewer pipe with some of it dissolving into condensation on the concrete surface. Here, where there is both a source of oxygen and sulphide *Thiobacilli* are able to generate sulphuric acid. This mechanism has been responsible for catastrophic failure of the sewer system in Hamburg, Germany (Rogers et al 1993a).

Nitric acid attack is similar to sulphuric acid attack in that a bacteria catalyses the generation of acid through the oxidation of a reduced compound during its growth. This is classically caused by two groups of bacteria collectively known as nitrifiers. The first group oxidises ammonia to nitrite and the second nitrite to nitrate. Both reactions liberate hydrogen ions and generate nitrous and nitric acids respectively. The bacteria responsible for these reactions are common in soils and aquatic environments such as river beds. Unlike the sulphur oxidising bacteria, the nitrifiers and specifically those responsible for ammonia oxidation, are sensitive to low pH's. This means that nitrogen base MID is self-regulating and does not generate the low pH's associated with the growth of *Thiobacilli* species.

Nitrifiers have been isolated from corroded concrete and implicated in the corrosion of stone with acid depleting the binding material (Rogers et al 1993a). A classic example of nitric acid MID has occurred on Cologne cathedral and other sandstone buildings in Germany (Rogers et al 1993a).

The bacteria responsible for the generation of organic acids are a much more diverse group than those discussed up to now in this section. These heterotrophic bacteria generate energy for growth through the consumption of complex organic compounds and may generate a wide variety of organic acids as by-products of their growth. These acids include acetic, lactic, citric, gluconic etc, all of which may attack cement-based materials. The wide variety of organisms, which fall into this category, means that they are very widely distributed in all environments, particularly soil. The role of heterotrophic bacteria in MID is not as extensively studied as that of the sulphur oxidisers or the nitrifying bacteria. However, they have been isolated from concrete corrosion sites and it is suggested that they play a role in reducing the pH to a value, which is more favourable for the growth of *Thiobacilli* species (Rogers 1993a).

### Generation of Complexing Agents

From the point of view of radioactively contaminated concrete, organic acid attack has an additional effect which may be important. This is the fact that these acids and particularly citric acid, can complex radionuclides resulting in an increased solubility. In the case of citrate plant roots and fungal hyphae have been implicated in its release into soils (White et al 1997). The degree to which complexation is a factor will depend on the manner in which the radionuclides are immobilised on the concrete surface. It is possible that the action of direct acid attack and complexation act in concert. With the acid attack resulting in the radionuclides becoming more susceptible to complexation since their attachment to the concrete is weaker.

In addition to the organic acids, micro-organisms are known to produce a whole range of organic molecules which can complex metals. These include siderophores which are specifically excreted under iron limiting conditions, and metal binding proteins such as metallothioneins. The extent to which these compounds are important in the mobilisation of radionuclides is difficult to assess and their generation may be a source of significant uncertainty. However, 2-ketogluconic acid has been implicated during the weathering of silicates (Webley et al 1963) and oxalates during basalt weathering (Silverman and Munoz 1970). Complexation by these compounds cannot therefore be neglected in consideration of risks.

## Factors Influencing Biodeterioration

In order to assess the impact of biodeterioration on concrete and the release of radionuclides it is important to understand the factors which control biodeterioration. Although the surfaces on which micro-organisms are growing during MID are generally inert the organisms must be in contact with an environment which provides them with the nutrients they require to grow. The major controlling factors for biodeterioration are outlined below.

### *Water availability*

Water is essential for microbial growth, consequently without an adequate amount of water MID will not proceed. This water may be provided as a liquid or a vapour and could come from the surrounding soil for a buried structure or from humidity for an above ground structure. The influence of water on the extent of MID is such that it may proceed intermittently in environments where there are pronounced wet and dry seasons.

Water logging can also have a marked effect on the activity and types of micro-organisms present in soil. This is because under these conditions oxygen generally becomes limited and anaerobic conditions prevail. This would promote the generation of organic acids such as acetic acid but retard *Thiobacilli* species and nitrifiers.

### *pH*

The pH can have a significant effect on the growth of micro-organisms with each species having a specific range and optimum under which it grows. As we have already discussed the pH range for *Thiobacilli* species and therefore sulphuric acid attack is very wide, whereas that for nitrifiers and nitric acid attack is narrower. In the case of concrete degradation the surface pH may have to be lowered through carbonation for example, before *Thiobacilli* species can take hold. This lowering of the initial pH may also be achieved by the presence of heterotrophic micro-organisms generating organic acids.

### *Nutrients*

The availability of nutrients is key to the progress of MID. If there are no reduced sulphur sources or reduced nitrogen source available then MID via *Thiobacilli* species or nitrifiers will not proceed. On the other hand if there is insufficient oxygen, then the availability of these sulphur or nitrogen compounds will not be important since the system will be oxygen limited. In terms of heterotrophic generation of organic acids the key will be the availability of organic substrates in the soil to drive the generation of the acids. The most important variable in assessing the likelihood of the various types of MID is therefore the availability and quantity of the particular nutrients required to drive the process.

The situation with the complexing agents may be more complex. This is because some of these compounds are generated by micro-organisms in response to nutrient shortages and in effect represent a survival strategy.

### ***Temperature***

As with pH micro-organisms have a optimum and a range of temperatures over which they grow Under environmental conditions the general trend is as the temperature increases so does microbial activity As with water availability this may have the effect of producing seasonal variations in the extent and rate of MID

### ***Presence of Micro-organisms***

Generally the presence of the particular microbes associated with MID is not a controlling factor This is because all the organisms involved are ubiquitous in all natural and man made environments In many cases they have the ability to stay dormant for long periods of time until the conditions which are favourable for their growth become available

### ***Colloid Generation in Cementitious Systems***

Very fine-grained suspended solid material can potentially act as a separate transport mechanism for radionuclides to that of dissolved species transport Plutonium and other actinides may form aggregates of polymeric aqueous species (true colloids) and these are discussed in the section on speciation Radionuclides may also be transported as sorbed material onto inorganic(mineral) and organic particulates (pseudocolloids) Such material is typically in the size range 1nm - 1 $\mu$ m (Kim *et al*, 1997) A number of studies of natural groundwaters including analogues of actinide contamination have shown that a significant proportion of radioactivity can be present in groundwater present on such pseudocolloids (Olofsson *et al*, 1986, Kim *et al*, 1987, 1989, 1997, Longworth *et al*, 1989, Miekeley *et al*, 1989, Dearlove *et al*, 1989) Colloidal material which has been shown to sorb actinides includes, organics (humics), iron hydroxides, clay minerals, silica, and other silicate minerals (feldspar)

Direct investigation and characterisation of colloid formation in cementitious systems has been made by Ramsey *et al*, (1988)(see also Gardiner *et al*, 1997) Colloids formed in leachates from OPC were filtered to collect various size fractions and were examined by electron microscopy, X-ray diffraction and bulk chemical analysis (ICP-AES, ICP-MS) Colloids collected were composed of CSH and effectively represent fine - grained cement matrix Colloids produced showed significant sorption of radionuclides including uranium Leaching of OPC in these experiments was performed in closed flasks purged with nitrogen, thus eliminating carbonation, it would be expected that fine-grained suspended CSH material would undergo carbonation in an open system with freely available CO<sub>2</sub> During carbonation CSH produces amorphous silica which may form colloidal material

In order to increase radionuclide mobility significantly sufficient colloid particles must be present in suspension Gardiner *et al*, 1997 have considered the processes controlling colloid particle growth and aggregation, nucleation, temperature and ionic strength are factors which govern the colloid concentration in experiments on colloid generation from OPC leachates Gardiner *et al* comment that when included in the Nirex 97 risk assessment of the post-closure radiological safety case of a U K repository cement generated colloids did not significantly increase risk Bradbury and Sarott (1994) also comment on the ability of

cementitious colloids to significantly increase the total concentration of radionuclides in the aqueous phase of the near-field repository environment, since CSH is the major component of both colloids and cement solid phase sorption properties will be similar. Bradbury and Sarott (1994) conclude that unrealistic amounts of colloidal material ( $> 10$  grams/litre) will be necessary to significantly increase aqueous phase radionuclide concentration. Similar arguments may apply to the generation of colloids from carbonated concrete if it can be demonstrated that the solid substrate and colloid material are composed of similar materials.

### ***Ancient analogues of concrete degradation***

Ancient analogues of modern OPC based concretes have been examined to provide information on the long-term behaviour of concrete and mortar in radioactive waste repositories (Lagerblad & Tragardh, 1996). The greatest difficulty in applying such information is the variation in the composition and grain size of ancient cements. Portland cement used in the early 20th century were coarser and contained a higher content of  $C_2S$  than that used today. OPC based cements exposed to water for periods of the order of 100 years remain durable, there is evidence that cement phases requilibrate and form larger crystals, and in some cases there is evidence of reaction with cement aggregates. Available examples show relatively little carbonation when immersed in water (5mm in 90 years, Lagerblad & Tragardh, 1996). More ancient Roman mortars and concrete over 2,000 years old which contained pozzolanic material resembling OPC type cements still show strong durability (Jiang and Roy, 1994). These cements are fully carbonated and contain only a small amount of calcium silicates (Majumdar et al, 1988). Carbonation occurs in these ancient buildings because of exposure to the atmosphere (Lagerblad & Tragardh, 1996). Modern pollution, in particular acid rain, has had a marked influence on the durability of some ancient monuments such as the Taj Mahal and the Pyramids (Roy and Jiang, 1997) and indicates the importance of modern sulphate and nitrates to concrete degradation.

### ***Repository degradation models***

Long-term models have been devised to predict the structural and chemical evolution of concrete structures for low and intermediate level radioactive waste disposal. Models have been proposed of varying detail, and considering various chemical and physical processes of cement and concrete degradation. Lagerblad & Tragardh (1996) have produced a conceptual model for the chemical and structural evolution of a proposed Swedish deep nuclear waste facility. This model identifies the processes and estimates the extent of chemical degradation during the periods of site development and post-closure, where differing groundwater, headspace gas composition and temperature conditions occur. For this deep repository extremely long time-scales, of more than 100,000 years, are considered and only a qualitative description of the behaviour of concrete is provided. Mathematical models have been developed to quantitatively predict the service life of concrete buried near to the surface over periods up to 1000 years used to store low-level radioactive waste (Atkinson and Hearne, 1989, Reed et al, 1994 report, Snyder et al, 1996, Gerard et al, 1997, Lee et al, 1995). Most of these models utilise empirical analytical equations to model individual degradation processes such as sulphate attack,  $Ca(OH)_2$  leaching, and carbonation. Corrosion of steel rebar can be modelled by considering the diffusion of chloride to the steel and from an anoxic corrosion rate. The model of Reed et al (1994) links these degradation processes to a structural analysis code which computes stresses in concrete and weakened rebar at various locations in a structural model. Once stress in the rebar exceeds a certain threshold cracks develop in the concrete as a function of the structural design, at a higher threshold the rebars yield and additional stress is applied to other parts of the structure. The model successively calls the concrete degradation and structural sub-models until some predefined state of collapse of the structure is reached. Snyder et al (1996) consider the



advective and diffusive transport of ions through a repository concrete slab and its associated degradation by sulphate attack, steel corrosion and  $\text{Ca}(\text{OH})_2$  leaching Gerard *et al* (1997) consider simultaneously the specific interactions between diffusion, leaching, mechanical strength, cracking and permeation Alcorn *et al* (1990) have derived a model to predict the hydraulic conductivity of OPC cement grout to be used as a cement backfill material, according to this model for an ambient hydraulic head of 1m/m the hydraulic conductivity remains below acceptable performance level ( $10^{-10}$  m/sec) for a minimum period of 30,000 years Adenot and Richet (1997) describe a model of purely diffusive reaction of water with cement paste which incorporates the chemical leaching behaviour of CSH and the breakdown of monosulphate and ettringite According to Adenot and Richet (1997) for a good quality cement (water/cement = 0.4) a degradation layer composed of CSH and silica gel will extend a thickness of 1.2 mm after 3 months and 4 cm after 300 years Purely diffusive alteration of cement is limited by the build up of a protective layer of silica gel, if this gel is removed by some other process such as erosion or chemical dissolution then degradation is more severe

### **Concrete degradation relevant to radionuclide mobility at Rocky Flats**

Concrete degradation effectively controls release of actinide contamination by allowing free access to moving groundwater Concrete has a low permeability compared to soil material and therefore it is unlikely that there will be significant water flow through concrete blocks buried with soil, flow will concentrate around the outside of concrete blocks The bulk of the contamination in RFETS concrete is present in the upper few millimetres of concrete The mobility of radionuclide contamination will therefore be primarily controlled by the zoned chemical degradation formed on the surface of the concrete The nature of the degradation will clearly depend on the groundwater environment and geochemistry

The background groundwaters at RFETS within the upper hydrostratigraphic unit are typical dilute Ca bicarbonate waters, whereas groundwater at depth in the lower unit are more sodium rich and more variable The upper hydrostratigraphic unit is variable in thickness from 10 ft to 130 ft therefore it is likely that buried concrete will be in contact with a dilute Ca bicarbonate water Such water is unlikely to produce enhanced degradation of AFm phases in the cement matrix by attack by sulphate, chloride or magnesium In the industrial area however, there are some high concentrations of sulphate over 1000 mg/l, these concentrations are likely to produce enhanced degradation by formation of secondary ettringite Concrete buried in the unsaturated zone is likely to be subjected to carbonation  $\text{CO}_2$  partial pressures in soil gases are typically above that of the atmosphere as a result of respiration by plants and micro-organisms, and thus carbonation will probably be accelerated during burial Partial pressures of  $\text{CO}_2$  calculated from speciation calculations are not summarised in the RFETS Site Characterisation Report (EG&G, 1995) The example WATEQF output in Appendix H of the Groundwater Geochemistry Report however gives a  $\text{CO}_2$  partial pressure of  $6.93 \times 10^{-2}$  atm which is above the maximum of  $\text{CO}_2$  levels normally measured in soils ( $\log p\text{CO}_2 = -1.5$  Appelo and Postma, 1994) While this value may not be typical  $\text{CO}_2$  contents are likely to be significantly above that of the atmosphere, and will thus promote carbonation Fujiwara *et al* (1992) examined concretes buried in soil for 60 years in saline groundwater, they observed that calcite was the main alteration product in the upper 10 cm of the concrete, and that chloride alteration occurred at greater depth as a consequence of the saline water The samples examined by Fujiwara *et al* were in saturated water where carbonation is generally thought to be less effective More ancient Romanic concretes and mortars are virtually completely carbonated on exposure to atmospheric  $\text{CO}_2$  There seems little doubt that the main chemical alteration of the surface contaminated layers of concrete at RFETS will be by carbonation

As discussed previously, carbonation results in a significant decrease in pH from above 10.5 for buffering by CSH and  $\text{Ca}(\text{OH})_2$  to around 7-8 buffered by calcite (Figure 1), this has important implications for the solubility and sorption of Pu, U and Am. In general carbonated, weakly alkaline cements do not perform as well as fresh high pH matrices in immobilising nuclear waste (Glasser, 1997). Carbonation of the surface of concrete results in a decrease in void space and an increase in durability. Carbonation may therefore physically entrap particulate oxide contaminants, this could possibly have occurred already by atmospheric carbonation, or may occur subsequent to burial.

Controls on the redox state of groundwaters at RFETS are largely undefined (EG&G, 1995), few reliable Eh measurements are available. Field measurements do record dissolved oxygen, but reduced iron minerals such as siderite and pyrite and carbonaceous materials are identified in cores from the upper hydrostratigraphic unit (EG&G, 1995), such observations are typical of the disequilibrium of redox reactions in natural groundwater (Stumm and Morgan, 1981). Corrosion of steel rebar exposed to groundwater in demolished concrete will act as a reductant to produce reduced groundwater conditions, the effectiveness of this reductant will depend on the groundwater flux, the rate of corrosion and the dissolved oxygen content of the inflowing groundwater. It has been discussed how microbial activity can effectively catalyse redox reactions and hydrogen produced by anaerobic corrosion could be utilised by sulphate reducing bacteria, and could conceivably reduce available sulphate, particularly in the industrial area where 1000 mg/l sulphate is measured. Given the large climatic variation at RFETS seasonal variations could conceivably result in cyclic reduction and oxidation of sulphate which gives rise to the classic sulphuric acid mediated form of microbial induced degradation (Rogers *et al*, 1993a). Sulphide is however likely to precipitate as iron sulphide if associated with steel corrosion and may not be available for subsequent oxidation by *Thiobacilli*. Since sulphides are present in the local alluvium and bedrock, and there is no recorded evidence of sulphide oxidation then it would appear that microbial influences on cement degradation and controlling redox state are limited at RFETS. Unless some other form of reduced substrate such as organic matter is disposed with buried concrete then it is likely that the prevailing background Eh will continue to apply.

Modelling studies of the behaviour of large concrete structures used in near-surface low-level radioactive waste disposal repositories indicate that their gross structure will survive intact for periods of around 1000 years (Reed *et al*, 1994, Gerard *et al*, 1997). After this time severe cracks will have developed allowing groundwater access to radioactive waste. Buried concrete rubble at RFETS will not be subject to the same stresses as large intact structures, which promote the cracking and breakdown of large structures. Degradation of buried concrete will be predominantly by microscopic-scale chemical and physical processes which will eventually lead to spallation of surface layers, where particulate and liquid contamination is concentrated. The diffusion controlled cement degradation modelling of Adenot and Richet (1997) is more applicable to the degradation of buried concrete rubble since this describes the chemical degradation of the concrete surface exposed to a reactive fluid. Considering that groundwater flow will be around concrete blocks rather than through the cement microporosity, diffusion will likely control the cement degradation reactions. Adenot and Richet (1997) predict that for pure water diffusive degradation will extend 4 cm after 300 years in good quality concrete. Carbonation, which is expected to be the dominant degradation processes for buried concrete at RFETS, is likely to produce more aggressive alteration, although carbonation will tend to reduce permeability in the concrete surface and hence reduce diffusion. Considering these modelling studies and evidence from ancient cements it is likely that chemical degradation will extend a distance of the order of 10 cm during the 1000 year risk assessment period, which will include the majority of the surface contamination. Uranium present in the aggregate is unlikely to be exposed to free-flowing groundwater during the 1000 year risk assessment period.

Spallation of the surface layer will increase the accessibility of groundwater to radionuclide contamination. Spallation is dependant on the nature of the degradation mechanism, carbonation improves durability and reduces the susceptibility to freeze-thaw mechanisms. Sulphate attack and accelerated leaching by microbial activity breaks down the cement matrix allowing disaggregation of the surface layer.

Possible colloidal materials generated from cement degradation are silica resulting from leaching and carbonation of CSH and iron hydroxides produced from steel corrosion. Natural colloids may exist in the background groundwater in forms such as humics or suspended clay particles derived from weathering and erosion of bedrock claystones. The additional effects of colloids generated from cement degradation should be assessed with reference to these background colloids, and to competition for sorption of radionuclides between colloids and the concrete matrix (Bradbury and Sarrott, 1994).

## Leaching of Actinides in Cementitious Systems

Direct experimental measurement of the leaching and diffusion of actinides in cementitious systems is much more limited than that of more mobile radionuclides such as cesium. The Swedish Nuclear Fuel and Waste Management Company (SKB) have undertaken research, from 1980 to 1990, and the results have been summarised by Albinsson et al (Albinsson et al, 1993). The experiments described in this work involved the measurement of cesium, americium and plutonium diffusion into five different types of concrete. The experiments were carried out over long time scales, 25 years for americium and 5 years for the plutonium.

The experimental technique involved taking pre-aged concrete samples, with approximate length of 25 mm. The samples were then dipped into radionuclide-spiked porewater, inside a glove box to avoid significant uptake of carbonate. At the end of the experiments, the concrete samples were ground, removing a 0.1 - 0.7 mm layer with each grinding. Estimation of apparent diffusivity ( $D_a$ ) was achieved either through activity measurements or, more accurately, through autoradiograms.

The result was that no movement of plutonium or americium could be measured (0.2 mm), despite the long time scales. The  $D_a$  for americium from activity measurements was estimated at  $1 - 9 \times 10^{-16} \text{ m}^2/\text{s}$ , while autoradiogram measurements indicated a  $D_a$  of  $< 0.3 - 1.8 \times 10^{-17} \text{ m}^2/\text{s}$ , with the variation mainly depending on how deep the grinding was, rather than the type of concrete used. The Plutonium  $D_a$  was similarly low, with a range of values given by  $0.8 - 2.4 \times 10^{-17} \text{ m}^2/\text{s}$ , from activity measurements. No autoradiograms could be taken, as almost all the activity was removed after the first grinding.

The explanation for the low diffusion of these actinide elements is their high sorption onto concretes. The  $R_d$  for americium sorption onto concrete varies between 1 and  $10 \text{ m}^3/\text{kg}$ , while the plutonium sorption is slightly lower ( $R_d = 1$  to  $5 \text{ m}^3/\text{kg}$ ). The higher sorption exhibited by americium would suggest that its  $D_a$  should be lower than plutonium, when in fact the reverse is true. This may suggest that the sorption - only mechanism is not the whole story. However, the fact that sorption is so high, and that the differences between the two actinides is small, means that the evidence is not clear-cut.

European Community sponsored research has also focused on the leaching behaviour of radionuclides from cemented waste (Vejmelka et al, 1991). This series of experiments first looked at the behaviour of uranium, plutonium, americium and neptunium in cement samples, in a Q-brine ( $\text{MgCl}_2$  rich solution) and NaCl brine.

To accelerate the leaching process, crushed samples were used. The pH of the Q-brine/cement solution was found to be 6.5, while the NaCl-brine/cement solution was at pH 12.5. Plutonium loadings were varied between  $10^{-9}$  and  $10^{-5}$  g/g cement, neptunium between  $10^{-6}$  and  $10^{-4}$  g/g cement, and uranium from  $10^{-4}$  to  $10^{-1}$  g/g cement. These amounts roughly correspond to the levels found in real waste encapsulation.

The results showed, for the Q-brine solution, a linear increase in americium and neptunium aqueous concentrations with increasing actinide loading. This indicates that sorption is the dominant factor in the determination of aqueous concentration. The results for plutonium are not shown, but the text mentions that the same behaviour is observed for plutonium. Uranium exhibits similar behaviour below loadings of 0.01 g/g cement, above this concentration, a constant aqueous concentration of  $5 \times 10^{-5}$  M is observed, which corresponds to the solubility limit of  $\text{UO}_2(\text{OH})_2$ . This was confirmed by the presence of a yellow precipitate.

In NaCl solutions, the high pH means that solubility controls the aqueous concentrations of all of the actinides. The main conclusion from this portion of the work is that the concentration for Am, Np and Pu is limited to  $1\text{e-}8$  M to  $1\text{e-}10$  M (for both brines) and  $1\text{e-}5$  M for uranium.

An important conclusion is that the behaviour of the actinides is independent of the doping technique. Thus the same result is observed whether the actinide was incorporated into the cement or added later into the solution.

It was also discovered that the aqueous concentration of Am was not effected by the presence of cerium, indicating that cerium does not compete with americium for sorption sites, and that ion exchange is not a likely mechanism for radionuclide sorption onto cement materials.

The kinetics of leaching from cement encapsulated materials was also examined. For Americium, the composition of the brine had no effect on the leaching behaviour, while for plutonium, the low solubility of plutonium hydroxides meant that the experimental concentrations were below detection limits in the NaCl brine. The results showed that the effective diffusion coefficient for Pu was  $1 \times 10^{-16}$  m<sup>2</sup>/s, and for americium the value was  $2 \times 10^{-17}$  m<sup>2</sup>/s.

The leachability of Nd (an analogue of trivalent actinides), uranium, thorium and strontium have been examined in a CO<sub>2</sub> free environment (Serne et al, 1996). Crushed cement samples containing these four radioelements were placed in deionized water, and the aqueous concentrations measured at a range of pH's, and at different times. The results showed that equilibrium was reached, in all cases, within 2 days.

Neodymium aqueous concentrations fell steadily with increasing pH (from 7 to 9), and were at the analytical detection limits at pH's above 9. The solubility limits of  $\text{Nd}(\text{OH})_3$  were shown to approximate the observed results well. Similar results were observed for uranium, and the aqueous concentrations could be explained by the equilibrium with  $\text{CaUO}_4$ . Thorium aqueous concentrations were at or below the detection limit over the whole pH range, this is probably due to the formation of the insoluble  $\text{ThO}_2(\text{am})$  phase. Strontium leached concentration indicated no pH variation, but the prospect of precipitating strontium carbonates in a real groundwater system cannot be ruled out.

The conclusion from this work is that solubility, rather than adsorption is the dominant factor in determining leaching of actinides from cementitious materials, provided the contaminants are present at > 0.15% of the cement waste form.

## **Conclusions on Leaching Experiments**

It is difficult to make any firm conclusions based on the limited amount of data presented here. However, the following observations can be made:

- 1 The penetration of actinide elements into a cement waste form is limited, even when the radionuclides are initially in the aqueous phase. This supports the assumption that the contamination of concretes at RFETS will be surficial in nature, and concentrated within the first few millimetres of the concrete.
- 2 The factors controlling actinide leaching from concrete are solubility and sorption. The predominance of one over the other will depend on the concentration of each actinide originally present in the concrete.
- 3 The fact that the contamination at RFETS will be surficial, rather than analogous to encapsulated waste, and leaching determined by sorption and solubility means that sorption and solubility data from the literature can be used to estimate leaching. Diffusion processes are not relevant to this study.

## **Behaviour of actinides in cementitious environments**

The lack of much real actinide leaching data means that the chemical behaviour of the elements in a cementitious environment must be investigated to aid elucidation of likely leaching behaviour at RFETS. The limited site data suggests that the contamination is likely to be particulate, particularly  $\text{PuO}_2$ . Thus, the first factor in determining the leach rate from the surface of the concrete is the solubility of these minerals. Once in the aqueous phase, the actinides will come into contact with the cement matrix itself, with the possibility of sorption further retarding the movement into the groundwater.

Therefore, this section examines the available literature data concerned with actinide sorption and solubility in cementitious environments. A fully comprehensive review of the environmental behaviour of actinides is not reported here. Rather, the essential features of actinide solubility and sorption behaviour have been explored. From this, it is hoped, a preliminary picture of the factors influencing actinide leaching from concrete surfaces will begin to emerge.

## **Summary of Conditions expected in a cementitious environment**

The evolution of the chemistry in cement porewaters has been described earlier (Figure 1) and it has been concluded that carbonation will have a significant effect on the behaviour of concretes close to the surface. This impacts on radionuclide behaviour in two ways. Firstly, formation of calcite drops the pH of the porewater solution significantly to ~8, which could impact on radionuclide solubility and sorption. Secondly, the formation of calcite presents a different surface to the actinides, and a consequent change in sorption behaviour. Also, actinides form strong carbonate species in aqueous solution, and this can reduce sorption and increase solubility.

The redox conditions in the immediate environment of the contaminated concrete will also be an important factor in the determination of actinide leaching behaviour. The redox potential within the cement porewaters will depend on the composition of the cement. Ordinary Portland cements are poorly poised, and so the redox potential is easily influenced by the groundwater in contact with it. Cement blends containing significant amounts of blast furnace slag will produce reducing porewaters, due to the presence of iron sulphides, which

creates a  $\text{SO}_4^{2-}/\text{HS}^-$  poised system (as well as other sulphur couples) The result is a measured Eh of  $\sim 200$  mV (Glasser, 1991) However, it is unlikely that the concretes at RFETS will contain significant quantities of slag

Corrosion of the steel reinforcements is another source of potentially low Eh values As these rebars corrode, the Eh is lowered to hydrogen liberation potential This mechanism may lower the Eh of the bulk concrete porewater, however, the majority of the actinide contamination is on the surface of the concrete structures Therefore, it is more likely that the redox conditions of the concrete surface will mirror very closely the redox of the groundwater According to the geochemical characterisation (EG+G, 1995), the redox potential indicates slightly oxidising conditions (90 - 320 mV) Microbial activity could potentially lower this Eh on the concrete surface, but evidence for this is lacking at present

In summary, the actinides present on the surface of concrete at RFETS would, on burial, experience alkaline conditions, due to concrete degradation However, the influence of the groundwater is likely to be large, with carbonation of the concrete surface a very likely outcome The result would be a lower pH of  $\sim 8$  Redox conditions are likely to be mildly oxidising, due to the lack of redox poisoning from the concrete, and the consequent influence of the groundwater

### **Speciation of Actinides**

#### **General**

The actinide series of elements results from the filling of the 5f orbitals, the series beginning with thorium and ending with lawrencium The ionisation energies of the 5f electrons play an important role in the chemical behaviour of the actinide elements The ionisation energies of the actinide elements are significantly lower than those of analogous lanthanide elements, the reason being that the 5f orbitals are considerably more shielded from the nuclear charge than the 4f electrons Thus, the 5f electrons are less firmly held than the 4f electrons in the lanthanide elements, and so more available for bonding

The electronic structure has important implications for the available oxidation states for the actinide elements The similar energies of the 7s, 6d and 5f electrons means that multiple oxidation states are accessible, particularly for the first half of the series In contrast, the lanthanides are almost exclusively found in the 3+ oxidation state Table 1 (Katz et al, 1986) lists the oxidation states that uranium, plutonium and americium can form, with the most stable oxidation state indicated in bold

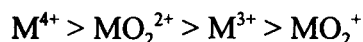
Element	Ground state electronic configuration	Oxidation states
Uranium	$[\text{Rn}] 5f^3 6d^1 7s^2$	3,4,5,6
Plutonium	$[\text{Rn}] 5f^6 7s^2$	3,4,5,6, (7)
Americium	$[\text{Rn}] 5f^7 7s^2$	3, 4, 5, 6

Table 1 Oxidation States of U, Pu and Am

The oxidation state of each actinide is crucial in the determination of its mobility In general, the reduced oxidation states are less mobile, exhibiting greater sorption and lower solubility (Choppin et al, 1995) Each element will also behave differently in terms of aqueous speciation, depending on the oxidation state

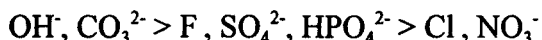
Actinides in the same oxidation state have the same structure. Actinide ions in the 3 and 4 oxidation states are in form of simple hydrated  $An^{3+}$  and  $An^{4+}$ , although these simple ionic forms have a strong tendency for hydrolysis and polymerisation unless in acidic solutions (Katz et al, 1986). Actinides in the higher oxidation states form oxygenated, actinyl species in solution,  $AnO_2^+$  and  $AnO_2^{2+}$ . These structures are very stable in aqueous solution, possess a linear structure (Greenwood and Earnshaw, 1984) and reduce the effective charge on the central actinide ion, for example, the charge on the Pu atom has been reported as +3.2 and +2.2 for the  $PuO_2^{2+}$  and  $PuO_2^+$  ions respectively (Silva and Nitsche, 1995).

Hydrolysis is an important reaction in natural waters, and has a large influence on actinide behaviour. In general, hydrolysis decreases in the order,



which is expected from charge to ion size ratios. Hydrolysis is important in that it can alter dominant oxidation states. For example, the greater hydrolysis of An(IV) species relative to An(III) results in greater stability for the An(IV) ion. Hydrolysis is also important in terms of the formation of polymers, (Pu colloids) with Pu(IV) being particularly susceptible (Toth et al, 1983, Choppin et al, 1995). Plutonium polymers are very stable and not easily depolymerised, and, as the effect of, for example, concentration, temperature and ionic strength is not well understood, the erratic nature of Pu(IV) aqueous solutions can make predictions of behaviour difficult (Katz et al, 1986).

The mobility of actinides in the environment is determined, to a large extent, by its solubility and sorption, and the results of specific experiments are presented in the following sections. The extent of both precipitation and sorption is influenced by aqueous complexation, which can reduce the extent of both processes. For example, the sorption of metals onto iron oxides is reduced in  $CO_2$  environment, at high pH, relative to sorption in a  $CO_2$ -free atmosphere (Waite et al, 1994). In general, the trend of strengths of complexation of various ligands with actinide ions is given by,



Thus, the main ligands that could perturb the sorption or solubility of actinides at RFETS will be carbonate, which is the dominant ion in RFETS groundwaters, and sulphate which is present in elevated concentrations at various locations (EG+G, 1995). Complexation of actinides by organic ligands is also well known (Katz et al, 1986) at RFETS organic ligands could be produced by microbial activity as described earlier, or by organic contaminants.

## Plutonium

Plutonium forms a number of oxidation states which are stable in natural waters. Pu(III) is stable under acidic conditions, although it is easily oxidised to Pu(IV).  $PuO_2^+$  disproportionates to  $Pu^{4+}$  and  $PuO_2^{2+}$ , although there is some evidence that it may be the dominant species in solution when concentrations are low, and the chances of two  $PuO_2^+$  ions interacting is very small (Choppin, 1983).  $PuO_2^{2+}$  is stable but can be easily reduced, even by the action of its own  $\alpha$  radiation (Katz et al, 1986). The dominant control of plutonium in natural waters is provided by the stability of the  $PuO_2$  phase (Stenhouse, 1995), with the degree of crystallinity being the dominant factor in controlling plutonium concentrations. The environmental behaviour of plutonium can be described schematically, as in Figure 4 (Choppin et al, 1995).

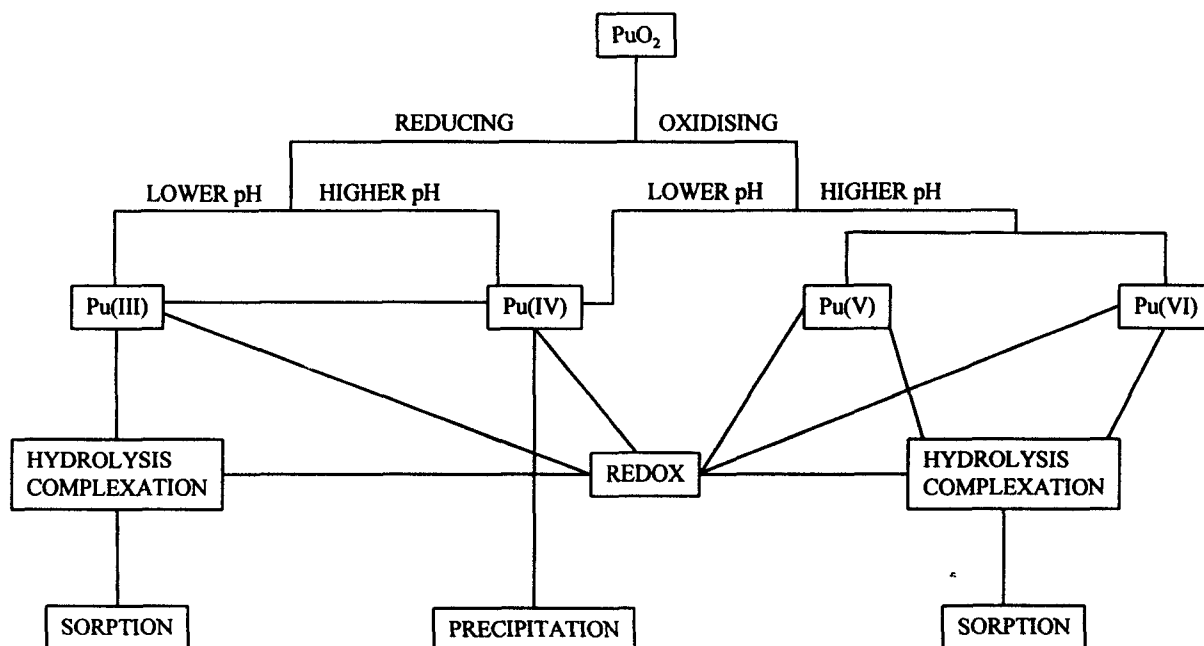


Figure 4. Schematic Representation of the Environmental Reactions of Plutonium

## Uranium

Uranium can form three stable oxidation states in natural waters,  $\text{U}^{4+}$ ,  $\text{UO}_2^+$  and  $\text{UO}_2^{2+}$ .  $\text{UO}_2^{2+}$  is the most stable form of uranium in aqueous solution, and is difficult to reduce (Katz et al, 1986).  $\text{UO}_2^+$  disproportionates to  $\text{U}^{4+}$  and  $\text{UO}_2^{2+}$ , while  $\text{U}^{4+}$  is stable with respect to water but is slowly oxidised by air to  $\text{UO}_2^{2+}$ . Rai et al (1990) note that oxygen fugacities must be below  $10^{-65}$  in order to maintain uranium in the U(IV) oxidation state.

The uranyl ion is the most stable actinyl ion, with a U-O bond distance of 180 pm (Greenwood and Earnshaw, 1984). Uranyl forms a large number of aqueous species, of which uranyl carbonates dominate at neutral pH in natural waters. Below pH 5, the uranyl ion and  $\text{UO}_2\text{OH}^+$  dominate aqueous speciation. The  $\text{U}^{4+}$ , like all  $\text{An}^{4+}$  ions, is easily hydrolysed above a pH of around 2.9 (Katz et al 1986), and its speciation is dominated by  $\text{UOH}^{3+}$  at low pH, and  $\text{U(OH)}_4^0$ , and possibly  $\text{U(OH)}_5^-$  (although the presence of this species has been disputed (Rai et al, 1990) at higher pH's).

Solubility control is sometimes difficult to assess due to the complex solid phase chemistry of uranium, with over 160 uranium containing minerals identified (Smith, 1983). Most of the uranium found in natural deposits is in the form of uraninite ( $\text{UO}_{2+x}$  ( $0.0 < x < 0.25$ )), indeed it was previously thought that all uranium was originally deposited as this mineral, with oxidation resulting in the formation of other minerals. Dissolution of uraninite under oxidising conditions can produce a whole wealth of secondary mineral phases, depending on groundwater conditions (see for example Finch and Ewing, 1992, Smith, 1983, Fayek et al, 1997, Sverjensky et al, 1992). This means that the solubility of uranium could be difficult to predict accurately in a complex environment.



## Americium

Americium is the simplest of the actinides looked at in this work as it forms only one oxidation state under natural conditions, Am(III). Other oxidation states are possible but require either very oxidising or reducing conditions (Katz et al, 1986)

Aqueous speciation is dominated by hydrolysis reactions and carbonation. It has been shown (Meinrath and Kim, 1991) that, under atmospheric conditions, hydrolysis dominates below pH 8, while at pH 8+ carbonate species are prevalent. Mixed hydroxy carbonate species are also possible (Silva and Nitsche, 1995)

## *Solubility of actinides in cementitious environments*

### Plutonium

The solubility of plutonium under cementitious repository conditions has been measured by a limited number of workers. The main problem in comparisons of solubility between workers is the crystallinity of the  $\text{PuO}_2$  solid phase. There is evidence that crystalline  $\text{PuO}_2$  is radiolytically transformed to a new hydroxide/oxide (Berner, 1995)

Ewart et al (1992) measured Pu solubility in a  $\text{Ar}/\text{H}_2$  atmosphere, to simulate the reducing conditions expected in a cementitious near field. Figure 5 shows the resulting solubility over a pH range of 7 - 12. As can be seen the solubility of Pu is low at pH's above 8, where the aqueous concentration is below  $10^{-10}$  M. The higher solubility at lower pH's is due to the formation of Pu(III) species.

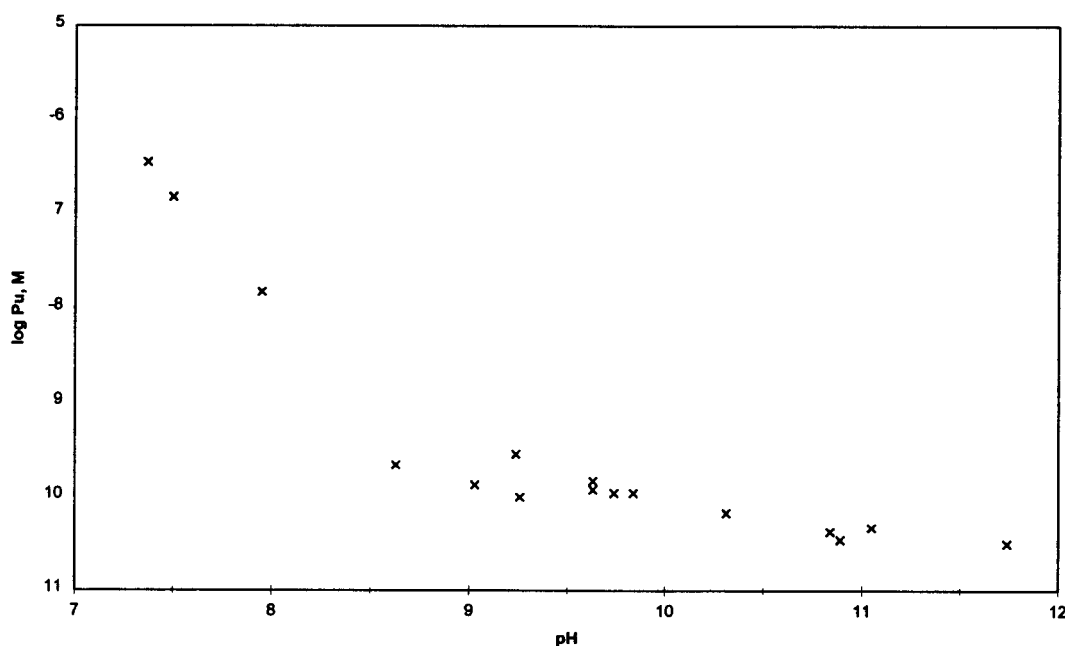


Figure 5 Measured Plutonium solubility under anaerobic conditions

Puigdomenach and Bruno (quoted in Berner, 1995) measured solubilities around  $10^{-10}$  to  $10^{-9}$  in the pH range from 8 to 10. Again, the solubility was seen to decrease linearly with pH below  $\sim 8$  (slope  $\sim 0.9$ ).

Measurements of plutonium solubility under aerobic conditions are more relevant to RFETS, and there are examples of these, of which only a selection is discussed here. In a study aiming to deduce the effect of asphalt degradation, plutonium solubility has been measured, at pH 12, in a concrete environment (Greenfield, et al, 1997). The resulting concentration was measured as  $1 \times 10^{-10}$  M, in good agreement with the results of Ewart et al (1992). Allard and Rydberg (1983) discuss plutonium solubility in both aerobic and anaerobic waters over a range of pH's. Under aerobic conditions, plutonium concentration is controlled by the solubility of  $\text{PuO}_2(\text{s})$ , with the dominant species (in the absence of carbonate) being  $\text{Pu}(\text{OH})_4^0$ . The solubility is constant between pH 5 and 10 (as Pu(III) species are less likely to form under aerobic conditions), with a concentration of  $10^{-9}$  M.

In the leaching experiments described earlier (Vejmelka et al, 1991), plutonium leachability was determined to be dependent on solubility limits at pH 12 -13, and the equilibrium concentration was determined to be  $1.6 \times 10^{-9}$  M, in good agreement with the results described above.

It has been discussed earlier that the impact of carbonation is likely to be significant at RFETS, and the effect on solubility needs to be assessed. Kim et al (1983) observed a large increase in plutonium solubility above pH 10, in solutions containing more than  $10^{-4}$  M carbonate. Kim et al (1993) proposed that  $\text{PuO}_2$  transforms into  $\text{Pu}(\text{OH})_2\text{CO}_3$  above pH 10, with this phase exhibiting greater solubility. The basis for this assumption is the drop in aqueous carbonate concentrations, indicating formation of a carbonate phase.

Yamaguchi et al (1994) also examined the effect of dissolved carbon on plutonium concentration, and they also observed increased solubility with increased carbonate levels (see Figures 6 - 7). However, Yamaguchi et al (1994) could find no evidence of carbonate uptake into a solid phase, instead they proposed that the increase in solubility is due to the formation of aqueous Pu hydroxycarbonate species. The mechanism is therefore in doubt, however the increased solubility is clear, and indicated that the leaching of plutonium from concrete surfaces will be enhanced in the presence of carbonate.

In conclusion, the solubility of  $\text{PuO}_2$  is low, even under oxidising conditions. The experimental determinations range from  $10^{-9}$  M to  $10^{-10}$  M. It must also be borne in mind that the crystallinity of the  $\text{PuO}_2$  solid phase is a crucial factor in determining the solubility of plutonium. The experiments described above used freshly precipitated or "amorphous"  $\text{PuO}_2$ . These will obviously be more soluble than crystalline  $\text{PuO}_2$ , and so the solubility limits could be viewed as maximum values. However, the effect of  $\alpha$  - decay can disrupt the crystal structure, reducing the crystallinity of the solid.

In the presence of carbonate, the solubility rises seemingly linearly above bicarbonate concentrations above  $10^{-4}$  M (at pH's below 10) and above carbonate concentrations of  $10^{-3}$  M, above pH 12.

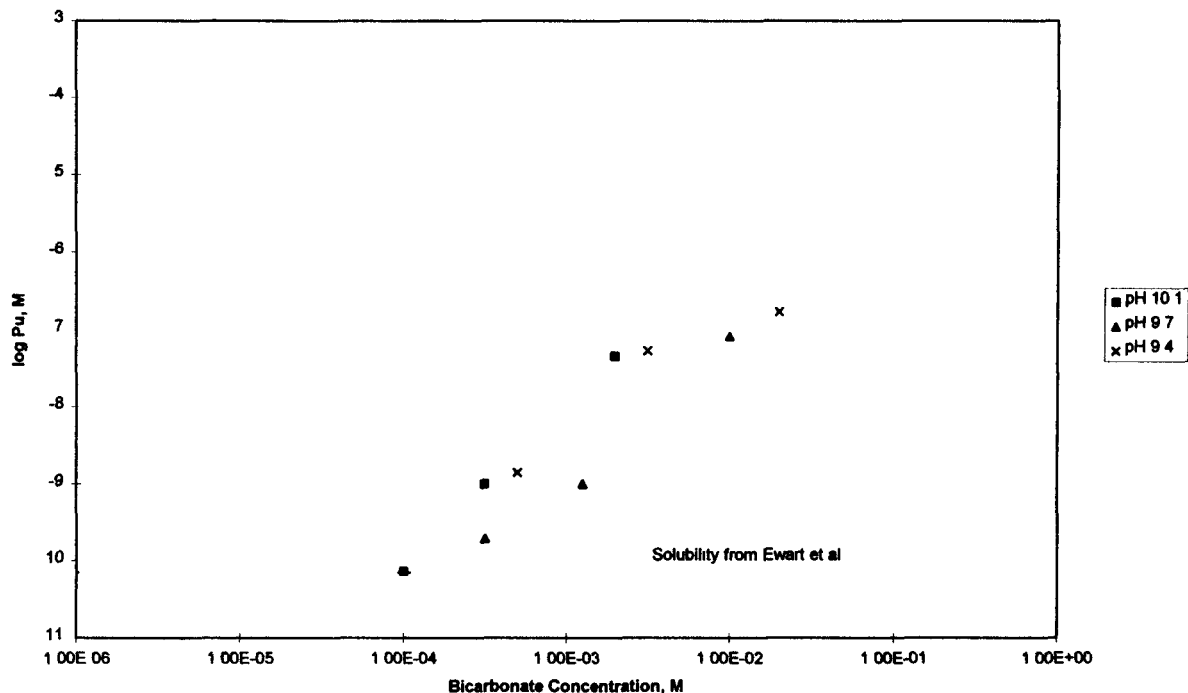


Figure 6 Plutonium Solubility as a function of carbonate concentration at pH 9.4, 9.7 and 10.1

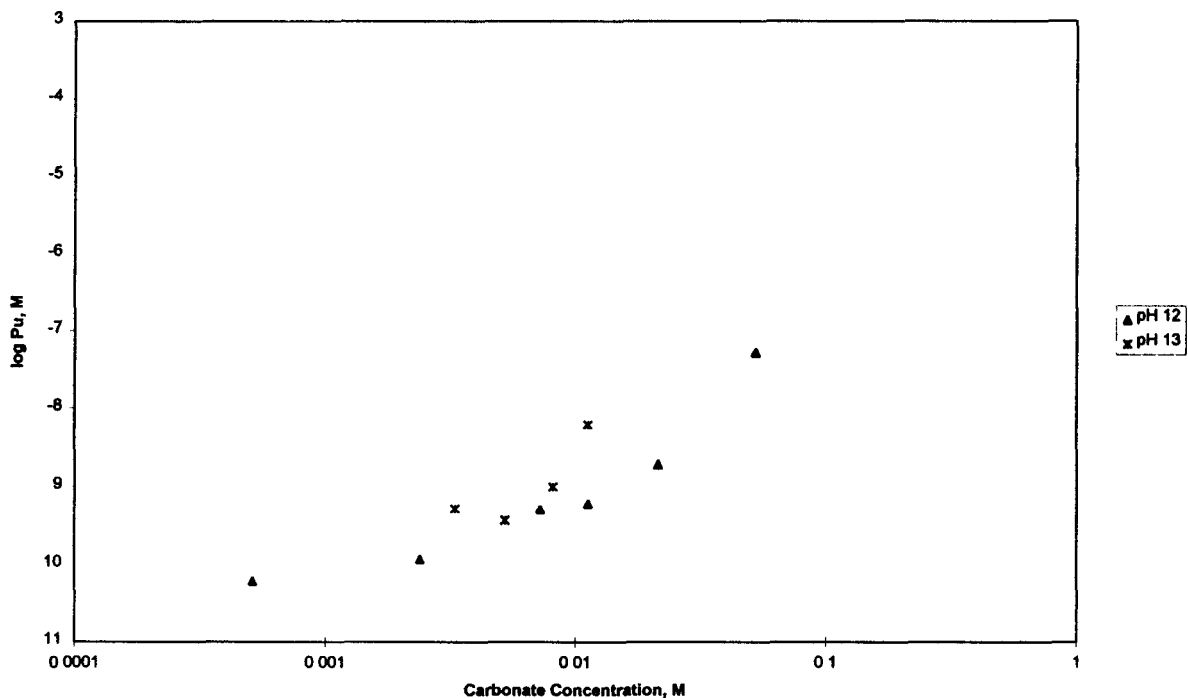


Figure 7 Plutonium Solubility as a function of carbonate concentration, at pH 12 and 13

## Uranium

The form of uranium contamination at RFETS is not known, but may be particulate or part of the concrete aggregate, and so solubility data for uranium both in terms of  $\text{UO}_2$  and other minerals, has been consulted

The amount of available data is vast, and only a fraction is presented here, although it is hoped that the main features of uranium solubility, in a RFETS context, is preserved

The solubility of  $\text{UO}_2$  under reducing conditions has been measured by a number of workers, and the results from two studies (Rai et al, 1990, Yajima et al, 1995) are shown in Figure 8. Both sets of experiments were carried out in inert electrolytes. As can be seen, the solubility of  $\text{UO}_2$  is defined by two distinct regions. Below pH 4 - 5, uranium solubility increases with increasing pH, while from pH 5+, uranium solubility is fairly constant at  $10^{-9}$  M (Yajima et al) and  $10^{-8}$  M (Rai et al). A slight rise in solubility can be seen at pH's above 10. This could be due to formation of the  $\text{U}(\text{OH})_5^-$  species or partial oxidation of U(IV) to U(VI).

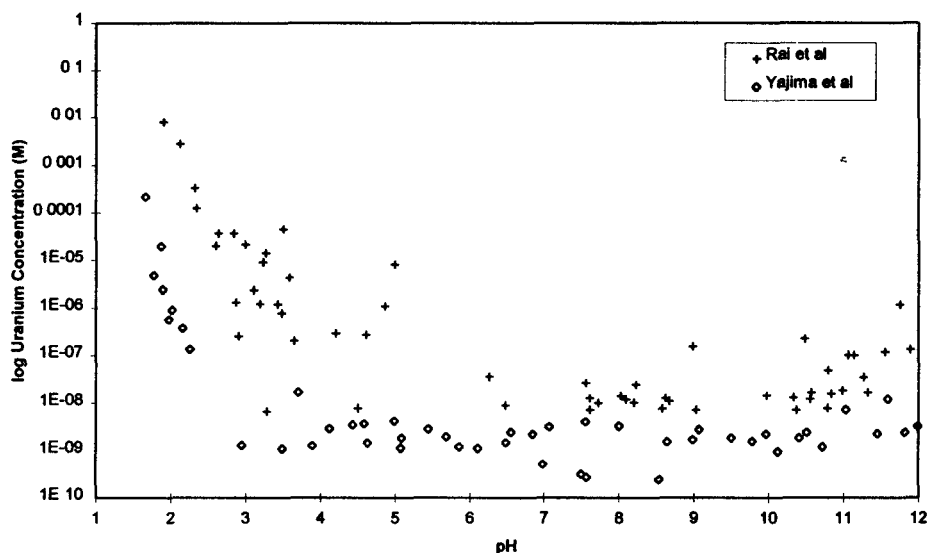


Figure 8 Measured solubility of  $\text{UO}_2$  under reducing conditions

Similar measurements were carried out by Ewart et al (1992), over a pH range of 5 to 13, with the solution composition approximated to a 9:1 Blast Furnace Slag / Ordinary Portland Cement leachate. These results showed a similar constant solubility over this pH range, although the measured aqueous concentrations are significantly higher than the concentrations shown in Figure 8 ( $3 - 2 \times 10^{-7}$  M). There was no evidence of increasing solubility at pH 10+, in contrast to the results shown in Figure 8.

The experimental evidence, therefore, seems to point to low solubilities for uranium under reducing conditions, ranging from  $2 \times 10^{-7}$  to  $10^{-9}$  M, and with no alteration of the  $\text{UO}_2$  phases. These experiments are useful in that they indicate the expected uranium solubility in well defined systems. However, the RFETS scenario calls for examination of uranium behaviour in the presence of groundwater ions, especially carbonate and under more oxidising conditions.

If the contamination of uranium at RFETS is in the form of particulate  $\text{UO}_2$ , the mechanism of dissolution under oxidising conditions can be complex.  $\text{UO}_2$  dissolution has been used as an analogue for the behaviour of spent fuel under repository conditions, and so its behaviour over a range of conditions has been examined by a number of workers (e.g. Casas et al, 1994, Torrero et al, 1994, Finch and Ewing, 1992, Wronkiewicz et

al, 1992) A general conclusion appears to be that at least two mechanisms account for the dissolution of  $\text{UO}_2$  under oxidising conditions Firstly, the surface of the  $\text{UO}_2$  is oxidised, and dissolves, releasing  $\text{U(VI)}$  into solution The second, slower mechanism involves the oxidation of the bulk  $\text{UO}_2$ , which subsequently dissolves The exact mechanism need not concern us here, but the implication is that it is the secondary minerals that control the uranium solubility under oxidising conditions Similarly, if the source of contamination is not  $\text{UO}_2$ , these secondary minerals will be the solubility limiting phases

The most apparently simple of the uranyl ( $\text{U(VI)}$ ) minerals are the uranyl hydroxides, such as schoepite, which is variously given the chemical formulae  $\text{UO}_2(\text{OH})_2$  or  $\text{UO}_3 \cdot 2\text{H}_2\text{O}$  It was this phase that was invoked by one of the leaching studies described earlier (Vejmelka et al, 1991) as the solubility limiting phase Schoepite exhibits the typical "U-shaped" solubility against pH behaviour, with a minimum solubility around pH 7 - 8, where the aqueous concentration equals  $10^{-5}$  to  $10^{-6}$  M (Torrero et al, 1994) and  $10^{-4}$  to  $10^{-5}$  M (Bruno and Sandino, 1989) The presence of carbonate, in even moderately low concentrations will tend to increase this solubility, due to the formation of uranyl carbonate aqueous species (Allard and Torstenfelt, 1985)

The presence of groundwater ions, such as carbonate, could result in the formation of other uranyl solid phases For example, Kato et al (1996b) found that the solubility limiting uranium phase under acidic conditions, with a 80% - 100%  $\text{CO}_2$  atmosphere, is rutherfordine ( $\text{UO}_2\text{CO}_3$ ), while  $\text{UO}_3$  was the solubility limiting phase at 0.99%  $\text{CO}_2$  atmosphere The solubility of this phase, as a function of  $\text{CO}_3^{2-}$  has recently been measured (Meinrath et al, 1996), and has been shown to be crucially dependent on the carbonate concentration, as would be expected

Cement leachates contain elevated concentrations of calcium, sodium, potassium and silica, and all of these species are capable of forming uranium solids Sandino and Grambow (1994) have shown that becquerelite ( $\text{CaU}_6\text{O}_{19} \cdot 11\text{H}_2\text{O}$ ) and compreignacite ( $\text{K}_2\text{U}_6\text{O}_{19} \cdot 11\text{H}_2\text{O}$ ) are formed quickly in the presence of calcium and potassium Similarly, Brownsword et al (1990) measured uranium solubilities in sodium and calcium hydroxide solutions, and found, above pH 7, a constant solubility of  $3 \times 10^{-6}$  M The results did not fit the expected behaviour for a schoepite type phase, and it was postulated that sodium and calcium uranates were being formed Recently,  $\text{Na}_2\text{U}_2\text{O}_7$  has been identified (Yamamura et al, 1997), as has the analogous  $\text{CaU}_2\text{O}_7$  solid phase (Heath et al, 1997) A leaching experiment described earlier (Serne et al, 1996) proposed that the observed concentrations of uranium were due to solubility limitations imposed by the  $\text{CaUO}_4$  solid phase, giving aqueous concentrations of less than  $10^{-8}$  M It must be borne in mind that no solid phase analysis was carried out, the conclusions were based solely on thermodynamic data and modelling and Berner (1992) calls into question the stability of the  $\text{CaUO}_4$  in alkaline solutions

Uranium alteration by silica is a possibility in cement porewaters Finch and Ewing (1992) note that schoepite is thermodynamically unstable in waters with even low activities of calcium and silica The mineral phase, uranophane ( $\text{Ca}(\text{H}_3\text{O})_2[(\text{UO}_2)(\text{SiO}_4)]_2 \cdot 3\text{H}_2\text{O}$ ) is one of the most common uranyl minerals, which may indicate that uranyl silicates are important phases controlling uranium concentrations in natural waters (Finch and Ewing, 1992) Other silicates, such as soddyite ( $(\text{UO}_2)_2(\text{SiO}_4) \cdot 2\text{H}_2\text{O}$ ) may also be important The formation of uranyl solid phases within a cement matrix have recently been examined (Moroni and Glasser, 1995), with several solubility limiting phases being identified These included becquerelite, uranophane and weeksite ( $\text{K}_2(\text{UO}_2)(\text{Si}_2\text{O}_5)_3 \cdot 4\text{H}_2\text{O}$ ) along with several unidentified phases Uranium solubilities are reported to be around  $10^{-8}$  to  $10^{-9}$  M, although it should be noted that the temperature in this study was  $85^\circ\text{C}$  More recently, a study examining the effect of silica on schoepite transformation (Sowder et al, 1996) found no evidence of

uranyl silicates being formed, even at silica concentrations of  $10^{-3}$  M. Instead, the presence of silica was seen to retard the transformation of schoepite to becquerelite in  $10^{-2}$  M and  $10^{-3}$  M calcium systems.

Berner (1992) modelled the solubility of uranium as a function of redox conditions, through consideration of uraninite,  $\text{CaUO}_4$ , uranophane and "x-phase" (basically a hydrated calcium uranate). He found that under extremely reducing conditions, uraninite is the stable phase, resulting in solubilities of  $10^{-8}$  to  $10^{-10}$  M. Under mildly reducing conditions, the solubility-limiting phase depends on pH, and modelled solubilities lie between  $10^{-7}$  to  $10^{-10}$  M.

The above discussion highlights the complexity of uranium in natural systems, and the uncertainty in knowledge of the identity of solubility controlling uranium solids under differing conditions. It does appear to be evident that the presence of cement leachates does lower the solubility from the value expected from schoepite equilibrium ( $\sim 10^{-5}$  M), whether through formation of calcium and/or silica phases. The presence of carbonate, however, appears to have the opposite effect, increasing uranium solubility, either through the formation of uranyl carbonate aqueous species or uranyl carbonate phases, such as rutherfordine.

### Americium

The solubility of americium will be dominated by the formation of hydroxide, carbonate and hydroxycarbonate minerals. According to Choppin et al (1995),  $\text{AmOHCO}_3$  limits the solubility of americium when  $[\text{CO}_3^{2-}]_{\text{free}} > 10^{-12}$  M (pH 6) and when  $[\text{CO}_3^{2-}]_{\text{free}} > 10^{-8}$  M (pH 8). The number of experiments dealing with americium solubility appear to be more limited than those for uranium, and a selection of these are presented below.

Atkinson et al (1988) measured americium solubility in cement equilibrated waters, between pH 8 and 13. The total carbonate concentration was  $3 \times 10^{-5}$  M. The results showed that the solubility was equal to  $\sim 10^{-8}$  M at pH's below 10, falling gradually to  $10^{-11}$  M at pH 13. The explanation given was the transformation of americium hydroxycarbonate into americium hydroxide, resulting in an inflection in the solubility curve. Similar results were observed by Ewart et al (1992) also in concrete equilibrated water.

The solubility of amorphous  $\text{Am}(\text{OH})_3$  in a carbonate free environment has been reported by Loida et al (1995), with the americium concentration equalling  $10^{-4}$  M at pH 7, dropping to  $10^{-9}$  M at pH 11. The crystallinity of the  $\text{Am}(\text{OH})_3$  is important, and Nitsche (1991) note that there is an order of magnitude difference between crystalline and amorphous  $\text{Am}(\text{OH})_3$  (e.g. at pH 7, solubility is  $10^{-3.5}$  M for the amorphous  $\text{Am}(\text{OH})_3$ , compared to  $10^{-4.5}$  for the crystalline solid). The experiments described earlier (Serne et al, 1996) showed that the leaching behaviour of neodymium (an analogue for americium) was controlled by the solubility of  $\text{Nd}(\text{OH})_3$ , with a solubility of  $10^{-5}$  M at pH 7, and a solubility of below  $10^{-8}$  M above pH 9. Assuming that the analogue between Nd and Am is a good one, this gives a good indication of americium leaching behaviour in a carbonate-free environment.

The effect of carbonation has been studied by a number of workers. Meinrath and Kim (1991) consider the formation of  $\text{Am}_2(\text{CO}_3)_3$  as the result of exposing americium to carbonated solutions. The resulting solubilities range from  $10^{-4}$  M (pH 6, carbonate  $10^{-7}$  M) to  $10^{-7}$  M (at pH 8, carbonate  $10^{-3}$  M). In contrast, Nitsche (1992) found that, in trying to prepare  $\text{Am}_2(\text{CO}_3)_3$ , orthorhombic  $\text{AmOHCO}_3$  formed in preference to  $\text{Am}_2(\text{CO}_3)_3$ . In addition, hexagonal  $\text{AmOHCO}_3$  was found to form in Yucca Mountain groundwaters, at pH 5.9 (Nitsche,

1991) (the orthorhombic solid formed at pH 7 and 8.4) The solubilities in these Yucca Mountain groundwaters was determined to be  $\sim 10^{-8}$  M, with solubility rising slightly as pH is increased

Other determinations of americium solubility includes Allard and Torstenfeldt (1985), where the calculated aqueous concentration was determined to be  $10^{-7}$  M in marl groundwater, and Vejmelka (1991), where the leachable concentration of americium was equal to the solubility limit at pH 12-13 ( $2 \times 10^{-10}$  M)

In conclusion, americium solubility is dependent on both pH and carbonate There is evidence of phase changes from americium carbonates, or hydroxycarbonates below pH 9, to  $\text{Am}(\text{OH})_3$  at higher pH Solubilities appear to vary from around  $10^{-5}$  M at neutral pH's to  $10^{-10}$  M at alkaline pH's

### **Sorption of actinides onto cements**

Sorption data is normally presented in terms of *distribution ratios*, or  $R_d$ 's (or  $K_d$ 's) The distribution ratio can be easily extracted from batch sorption experiments, through use of the following expression,

$$R_d = \frac{\text{Quantity of radionuclide sorbed per unit mass of solid}}{\text{Equilibrium concentration of radionuclide in solution}}$$
$$= \left( \frac{C_1 - C_2}{C_2} \right) \frac{V}{M}$$

where  $C_1$  = initial aqueous concentration of radionuclide  
 $C_2$  = final aqueous concentration of radionuclide  
 $V$  = volume of solution  
 $M$  = mass of solid phase

Cementitious materials are likely to be good sorption substrates for elements whose dominant sorption mechanism is surface complexation The specific surface area of cement materials are high, ranging from 55 to 200  $\text{m}^2/\text{g}$  (Lea, 1980, Bradbury and Sarott, 1994), suggesting that sorption capacity is high As has been described above, the actinide elements have a significant tendency to hydrolyse, with high first hydrolysis constants ( $K_{11}$ ), and high charge to bond length ( $z/d$ ) ratio (Baes and Mesmer, 1986) There is a strong correlation between distribution ratios on cement, and  $K_{11}$  and  $z/d$  values (Bradbury and Sarott, 1994) It would therefore be expected that uranium, plutonium and americium would exhibit high distribution ratios

The effect of cement composition needs to be addressed Several studies (Allard et al, 1984, Allard, 1985, Atkinson et al, 1988) have suggested that the specific composition of the cement has little or no effect on the sorption of readily hydrolysed elements, such as actinides There is evidence that the sorption of non-hydrolysed species such as Ra, Cs and I is crucially dependent on the cement composition (Heath et al, 1996, Holland and Lee, 1992, Glasser et al, 1997) In particular, the sorption of Cs (which is poorly sorbed by CSH phases) is claimed to be extremely sensitive to the composition of the ballast (aggregate) (Allard, 1985) or aluminium substitution into the cement (Glasser et al, 1997)

From the evidence, it appears that a good first approximation is that the specific cement composition has little impact on the sorption of actinides However, it must be borne in mind that most, if not all, of the experimental determinations of sorption onto cements were carried out at pH 12 and above At this pH, *and under the low carbonate levels considered*, actinides will be hydrolysed and sorption is likely to be close to

100% Under these conditions, variations in sorption due to the composition of the cement could be masked. If the porewater close to the surface of the concrete is influenced by the groundwater composition, pH will be lower than 12 and therefore, sorption may be lower and compositional variation more important.

Distribution ratios gleaned from the literature do indeed show high distribution ratios for actinides on cement. Below is listed a summary of some of the relevant  $R_d$  values for uranium, plutonium and americium onto cements.

Actinide	$R_d$	Comments	Reference
Uranium	0.1 - 6.3	Sorption onto seven cement blends, oxidising conditions	Allard et al, 1984
	8	U(IV) sorption value	Heath et al, 1996
	6.2	U(VI) sorption value	Heath et al, 1996
	0.1 - 2	Recommended values for oxidising conditions	Bradbury and Sarott, 1994
	1 - 5	Recommended values for reducing conditions	Bradbury and Sarott, 1994
Plutonium	1.2 - 12.6	Sorption onto seven cement blends, oxidising conditions	Allard et al, 1984
	10 - 30	Variation due to variation in solid-liquid ratio	Atkinson et al, 1988
	6.6	Pu(IV)	Heath et al, 1996
	1 - 5	Recommended values for both oxidising and reducing conditions	Bradbury and Sarott, 1994
Americium	2.5 - 25.1	Sorption onto seven cement blends, oxidising conditions	Allard et al, 1984
	7 - 60	Variation due to examination of particle size	Atkinson et al, 1988
	1 - 5	Recommended values for both oxidising and reducing conditions	Bradbury and Sarott, 1994

Table 2 Summary of distribution ratios for actinides onto cements

Thus, the actinides, particularly americium, apparently exhibit extremely strong sorption on cementitious materials. There is no apparent effect of pH, although the experiments were all carried out above pH values of ~12.5.

In explaining the sorption behaviour observed in these experiments, all of the authors have invoked surface complexation onto CSH phases as the most likely sorption mechanism. This is likely to be true for cements that have not been extensively leached or altered by interaction with groundwaters. Upon hydration, CSH forms on the outside of the cement powder particles, on the boundary between the interstitial water and the solid phases (Bradbury and Sarott, 1994). The CSH phase is almost amorphous and contains most of the microporosity of the cement. Accordingly, "much of the sorption potential associated with cement arises from the CSH micropore network and its concomitant high surface area" (Glasser, 1992).



However, the situation is likely to be different for a cement that has been leached, or more relevant to RFETS, carbonated. Carbonation results in the formation of calcium carbonate, which tends to fill space (and block cracks), and form a relatively dense skin of solids, effectively isolating the cement phases from the aqueous phase (Glasser et al, 1997). This means that calcium carbonate solids will become the dominant sorption substrate, with a resultant drop in sorption. For example, Stenhouse (1995) reports  $R_d$  values of 0.02 m<sup>3</sup>/kg, 0.4 - 5 m<sup>3</sup>/kg and 5 m<sup>3</sup>/kg for uranium, plutonium and americium sorption on calcite. These distribution ratios are significantly lower than corresponding cement  $R_d$ 's, particularly for uranium.

The precipitation of calcium carbonate minerals at the cement surface may induce the formation of co-precipitates with the actinide elements already present. Co-precipitation of trace elements within a calcium carbonate solid phase is a well-investigated phenomenon (e.g. Comans and Middelburg, 1987), with strontium predicted to be particularly effected (Plummer and Busenberg, 1987). An important consequence of co-precipitation is that, in contrast to surface sorption, the contaminant is held irreversibly, and so is inaccessible to the aqueous phase. This obviously has important consequences for the leaching of radionuclides from the surface of buried concrete, and therefore needs to be assessed.

Carlsson and Aalto (1996) have recently examined the co-precipitation of uranium with calcium carbonate. The results indicated that, under the experimental conditions (pH 9.6 and 8.5, in both nitrogen and CO<sub>2</sub> atmosphere) uranium did not co-precipitate with calcium carbonate. It was postulated that dominant species in solution, uranyl carbonates, were not of suitable size and charge to be incorporated into the calcite structure. This result confirmed earlier work by Carroll and Bruno (1991) which showed that co-precipitation did not occur over the range of experimental conditions.

In contrast to these experimental results, recent modelling work (Curti, 1998) predicts that the trivalent and tetravalent actinides will be significantly affected by co-precipitation with secondary calcium carbonate minerals. The implication to the behaviour of Pu(IV) and Am at RFETS is clear. However, this work must be viewed with caution. The results presented are purely the result of modelling, based on a simple distribution law model. This in itself is not reason to be cautious. However, the important parameter, the partition coefficient, has been estimated from consideration of the solubility products of pure metal carbonates,  $R_d$  values and the ionic radii of the metals. It is not clear at this point as to the validity of this approach, and experimental confirmation is required. The study does, however, emphasise the potential effect of calcite co-precipitation, and could be an important mechanism in the determination of leaching behaviour at RFETS.

The conclusion from this survey of sorption processes is that actinides are strongly sorbed onto cement phases, with americium particularly strongly sorbed. It would therefore seem that if uranium, plutonium and americium were sorbed onto the surface of concrete the concentration released into the aqueous phase will be limited. However, the surface of a buried concrete structure will be extremely susceptible to groundwater influences, particularly carbonation. Carbonation produces precipitates of calcium carbonate, for which the actinides have a lower affinity, resulting in less retention. Co-precipitation, which would effectively retard the release of contamination irreversibly, does not appear to be a viable mechanism for uranium, and, although a theoretical study has demonstrated the possible consequences for plutonium and americium, further experimental work is needed before firm conclusions can be made.

## Summary and Conclusions

A literature search and review has been undertaken regarding the processes controlling the behaviour of plutonium, uranium and americium in contaminated concrete at RFETS. The review has concentrated on two aspects: degradation of the concrete surface layer, where the bulk of the contamination exists, and a review of experimental studies of leaching of plutonium, uranium and americium from cement-based materials. It was quickly apparent that there was a significant lack of data on the latter. Consequently literature on radionuclide solubility and sorption have been examined to provide a background understanding of the behaviour of actinides in cementitious environments.

### *Concrete Degradation*

A review has been carried out on literature concerning the long-term degradation of cement and concrete used in radioactive waste encapsulation, and in repository structural designs, together with more general literature on the surface-dominated degradation of concrete and cement. The findings of this review have been considered together with site specific geochemical data to understand the likely behaviour of the surface layers of contaminated concrete, where the majority of the contamination exists.

The main form of concrete degradation occurring in RFETS concrete is likely to be carbonation of the surface. During this process carbon dioxide present in air, soil gas and dissolved in groundwater reacts with calcium phases ( $\text{Ca(OH)}_2$  and CSH) within the cement matrix to produce calcium carbonate and silica. Supporting evidence for this process comes from experimental studies, and examination of ancient analogues of modern OPC concrete. From modelling studies and examination of long-term carbonation it is likely that carbonation of the concrete surface will extend to a depth of around 10 cm in the 1,000 year period considered and will thus include the zone of contamination of plutonium, uranium and americium resulting from nitrate solution and particulates.

Since the background groundwater at RFETS is dilute other forms of concrete degradation such as sulphate and chloride attack are unlikely to be effective. In the industrial area of the site significant sulphate concentrations are measured (1000 mg/l) at which the ettringite form of sulphate promoted attack might be expected if these sulphate concentrations were maintained in the vicinity of the disposed concrete.

Other degradation processes to consider are the corrosion and expansion of steel rebars, which will produce cracking of large blocks of concrete, corrosion will occur at maximum rate since corrosion protection offered by the high pH of unleached concrete will not be effective in close contact with groundwater. Microbial induced degradation of concrete has been considered, particularly since the contamination is located at the concrete surface where microbial growth is most likely. There is however no clear evidence that microbial activity will be significant, although substrates for microbial growth are present at RFETS (e.g. pyrite, sulphate).

Degradation by carbonation is unlikely to disrupt the mechanical structure of the surface layers of concrete since the calcium carbonate formed is an effective cement which has been shown to survive for 2,000 years in ancient structures. Porosity is also reduced by carbonation which will reduce the effect of purely physical

degradation processes such as freeze-thaw Freeze-thaw and mechanical erosion of the concrete surface will be effective given the seasonal climatic variation and the topography at RFETS, such factors will also depend on the nature of disposal such as depth of burial Gross breakdown of concrete blocks is most unlikely over a period of 1000 years and thus access to uranium contamination in aggregate by groundwater will be restricted Growth of carbonate could conceivably entrap particulate contamination in the surface layer and restrict access by groundwater Degradation by sulphate attack or microbial action is more likely to disaggregate the surface layers of concrete and is likely to provide better access of groundwater to contamination Plutonium, uranium and americium contamination could be mobilised from the surface of concrete by colloidal material generated from concrete degradation The most likely colloids formed from degradation of RFETS concrete are silica colloids resulting from carbonation of CSH phases and iron hydroxide colloids formed from steel corrosion Studies of colloid formation in cement leachate has been examined in carbonate free experiments, however these are not applicable to RFETS as the CSH colloids produced are unlikely to be stable in the presence of carbon dioxide The ability of colloids to significantly increase radionuclide mobility in cementitious system has been brought into question recently

Chemical degradation of cement and concrete is critical to the mobility of plutonium, uranium and americium In addition to changes in cement mineralogy chemical degradation controls the composition of the local fluid which influences actinide solubility and sorption pH redox potential (Eh) and carbonate content are all important factors controlling solubility and sorption The most significant effect of concrete degradation is a reduction in pH from over 12 in fresh cement pore fluid containing free alkalis to pH~10.5 buffered by CSH phases and finally to a pH ~8 buffered by carbonate phases The aqueous carbonate content is controlled by CO<sub>2</sub> partial pressure which is influenced by external controls such as plant and microbial respiration in the soil zone and exchange with the atmosphere Cement and concrete will also regulate the CO<sub>2</sub> partial pressure in a closed system Degradation of the cement matrix is unlikely to influence Eh, however corrosion of steel rebars is likely to produce anaerobic conditions

Overall, from information in the literature it is possible to qualitatively predict the degradation behaviour of concrete at RFETS to provide background information for evaluating the chemical controls on leaching, solubility and sorption of plutonium, uranium and americium Some areas of uncertainty that have arisen during this review are

- Consideration of the effect of sulphate contamination in groundwater in the industrial area, is it representative of long-term composition?
- The potential role of microbiological processes in influencing concrete degradation and in controlling redox conditions
- The potential for generation of actinide sorbing colloids during carbonation of concrete

The lack of understanding of processes of redox control and colloid transport are uncertainties which are not necessarily confined to this study but are significant to radionuclide mobility in general at RFETS

### ***Leaching, solubility and sorption of plutonium, uranium and americium in cementitious systems***

Experimental measurements of the leaching of plutonium, uranium and americium from cement matrices are very limited in extent The main reason appears to be the low mobility of actinides in cementitious

environments, with a consequent need for long time scale experiments. Literature on radionuclide solubility and sorption have been consulted, to provide an understanding of the likely behaviour of actinides in a cementitious environment. From the results of this literature review, the following conclusions can be made.

Firstly, the penetration of uranium, americium and plutonium into intact concrete is very low, even when the radionuclides are in aqueous solution. This confirms the supposition that any concrete contamination at RFETS will be surficial. In addition, the low diffusivity means that any uranium present in the concrete aggregate should not leach into the groundwater, in significant quantities, over a 1,000 year time scale.

The diffusion coefficients presented by two sets of workers are reasonably consistent, especially so when the low mobility and thus difficulty in measurement is taken into account. The diffusion coefficient for plutonium was determined to be  $2 \times 10^{-17} \text{ m}^2/\text{s}$  (Albinsson et al 1993) and  $1 \times 10^{-16} \text{ m}^2/\text{s}$  (Vejmelka et al, 1991). For americium, the corresponding  $D_a$ 's are  $0.3 - 1.8 \times 10^{-17} \text{ m}^2/\text{s}$  (Albinsson et al, 1993) and  $2 \times 10^{-17} \text{ m}^2/\text{s}$  (Vejmelka et al, 1991).

The mechanisms controlling radionuclide leaching from cement or concrete are sorption onto the cement matrix and precipitation of solid phases. The dominant mechanism will depend on the initial concentration of the radionuclide. In general, radionuclides below the solubility limit will exhibit a linear increase in leached concentration, as sorption dominates (assuming linear sorption). Above a certain concentration, solubility limits will determine the leached concentrations, this value will correspond to the maximum extent of leaching, and will be fixed, unless geochemical conditions change.

The immediate environment of the concrete will be characterised by high pH, with the leachate containing elevated concentrations of calcium, silica and, initially at least, alkalis, such as Na and K. In addition, carbonation is likely to occur, inducing calcite precipitation. All of these factors, as well as the composition of the groundwater are likely to influence the leaching behaviour of the actinides.

The solubility of plutonium, uranium and americium, over a range of conditions, have been examined. In general, solubility is expected to be low at high pH's and low carbonate. Plutonium, for example, is likely to have a solubility between  $10^{-9} \text{ M}$  and  $10^{-10} \text{ M}$ . The effect of carbonation is likely to be crucial, with plutonium exhibiting increased solubility when bicarbonate concentrations are above  $10^{-4} \text{ M}$ . Uranium and americium are likely to change phases as a result of carbonation. The effect of calcium, silica and potassium on uranium solubility has been examined, with the conclusion that formation of phases such as uranophane will tend to reduce solubility. The formation of these phases under site specific circumstances, however, will have to be demonstrated. There is lack of data on similar phases of americium and plutonium, should they exist.

Sorption of actinides onto cements is likely to be high, as would be expected by easily hydrolysed elements, and  $R_d$  values are as high as  $30 \text{ m}^3/\text{kg}$ . All of the measured  $R_d$ 's have, however, been measured at very high pH's (12 - 13), which is more akin to the environment of cement - encapsulated waste. It is not clear whether these conditions will apply to the immediate environment of surface contaminated actinides. In particular, carbonation will result in the precipitation of calcite, which will present a new sorption substrate to the radionuclides. Sorption onto calcite appears to be less strong than sorption onto cement phases. The possibility of irreversible, co-precipitation of the actinides with calcite has to be considered. The experimental data suggests that co-precipitation of uranium (VI) with calcite does not occur, probably due to the size and charge of the uranyl carbonate aqueous species. However, it has been shown, theoretically, that co-precipitation could have a major impact on radionuclide migration.

From this literature review, it is clear that there are a number of dominant factors that will influence the leaching of radionuclide - contaminated concrete. A preliminary list of these factors is listed below,

- I Nature of contamination - this will determine the penetration of the radionuclide into the concrete (i.e. aqueous contamination will penetrate more deeply), and the initial solid phase present
- II The amount of contamination - different mechanisms (sorption or solubility) will operate at different concentrations. If the contamination is predominantly surficial, it is more difficult to define a g/g concentration
- III Geochemical Conditions - the conditions in the immediate environment of the contamination is crucial in the determination of leach behaviour e.g.
  - A interaction of the groundwater with the concrete and concrete porewaters
  - B pH and pe - the mobility of radionuclides in any environment is crucially dependent on these two parameters
  - C ligands - e.g. carbonate, calcium, alkalis, sulphate, organics
  - D alteration of cement minerals - co-precipitation
  - E nature of solubility limiting phase, if any

In summary, it is likely that the leaching behaviour of uranium, plutonium and americium, on purely chemical considerations, is controlled, ultimately, by the equilibrium with a solubility controlling solid phase. The exact nature of this solid phase, and the value for its solubility limit will be complex, and will depend on all the factors mentioned above.

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